Magnetic Field-Dependent Electronic Structures of Low Dimensional Organic Materials

David E. Graf
MAGNETIC FIELD-DEPENDENT ELECTRONIC STRUCTURES OF LOW-DIMENSIONAL ORGANIC MATERIALS

By

David E. Graf

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The members of the committee approve the dissertation of David Graf, defended on June 20, 2005.

James S. Brooks  
Professor Directing Thesis

Naresh Dalal  
Outside Committee Member

Nicholas E. Bonesteel  
Committee Member

Paul Eugenio  
Committee Member

Peng Xiong  
Committee Member

The Office of Graduate Studies has verified and approved the above named committee members.
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ABSTRACT

Organic systems provide the opportunity to study physics in lower dimensions. Rather than interactions between atomic sites, organic systems are comprised of molecules with the general shape of flat bricks. The stacking of these bricks produces a wide variety of structures with equally diverse ground states. The tau-phase molecular conductors are comprised of the asymmetric DMEDT-TTF molecule. These donors are arranged into a grid-like pattern to create two-dimensional planes of high conductivity. Materials based on stacks of perylene (Per) donor molecules have a conductivity anisotropy which makes them effectively one-dimensional and therefore susceptible to lattice instabilities.

Studies of these two very different species of organic charge transfer salts are reported in the following dissertation. Both materials undergo phase transitions in high magnetic fields. To better understand the ground state of the tau-phase materials, a wide variety of experimental techniques were employed. The donor molecules of the tau-phase systems, $\tau\text{-}(P-(S,S)-DMEDT-TTF)_2(AuBr_2)_{1+y}$ and $\tau\text{-}(EDO-(S,S)-DMEDT-TTF)_2(AuBr_2)_{1+y}$, only differ by the substitution of nitrogen for oxygen yet measurements reveal vastly different results. Measurements of magnetoresistance reveal metallic character in increasing magnetic fields followed by a rapid transition to a bulk insulator, followed by a large hysteresis as the material returns to a metal as the field returns to zero. Comparison between the above mentioned systems for magnetization and pressure dependence suggest a weakly coupled lattice for the nitrogen-based material, which distorts in high fields.

A systematic study of the perylene materials $(\text{Per})_2M(mnt)_2$ (where $M = \text{Au, Pt}$) offers an opportunity to observe the effects of high magnetic fields on the low temperature charge density state. With transition temperatures of 8 K and 12 K for $M = \text{Pt}$ and $M = \text{Au}$, respectively, readily available fields are capable of producing large changes in the states of the systems. $(\text{Per})_2\text{Au}(mnt)_2$ was chosen, at first thought, as an example of a “simple” highly anisotropic 1D system where an applied magnetic field closes the energy gap at a rate proportional to $B^2$. When the Au metal sites within the anion chains are replaced with Pt ($S = \frac{1}{2}$), magnetism is introduced to the system. At low temperature $M = \text{Pt}$ systems undergo both a Peierls and spin-Peierls transition at the same temperature. When $(\text{Per})_2\text{Pt}(mnt)_2$ is subjected to increasing fields beyond
~ 20 T, the conventional CDW is suppressed and a new density wave state is formed in high fields. Further measurements have been performed observing the change is the Fermi surface topology with the addition of pressure. We report on the field-induced density wave phase and its agreement with contemporary theories.
1.1 – Why Study Organic Materials?

The rich history of experimental research of organic materials stems from the relative ease with which one can vary experimental parameters and detect or produce a variety of interesting ground states. At low temperatures where thermal excitations are diminished, superconducting or insulating states, charge and spin density waves, or magnetically ordered phases are among the states that are observed. The possibilities seem to be limited only by the materials which can be synthesized.

Scientists have been studying organic materials for more than half a century. It was not until 1960, that Kepler [1] reported metallic behavior in a series of organic salts containing the anion TCNQ (tetracyanoquinodimethane). Later, this molecule was paired with TTF (tetrathiafulvane) to create TTF-TCNQ. Studies of the magnetoresistance of this material motivated the experiments which are reported in chapter 5. In the early 1980’s, the quasi-one-dimensional system (TMTSF)$_2$PF$_6$ was found to have a resistivity minimum four orders of magnitude lower than the earliest organic compounds. Jerome [2] discovered this to be the first organic superconductor, under a pressure of ~ 6 kbar, which created a surge of interest in these materials which has yet to subside.

The mostly commonly studied organic materials are the charge transfer salts (CTS). Each of these materials is produced by combining an electron donating cation and an acceptor. The charge transfer between the two molecules depends on the ionization potential of the donor, the electron affinity of the acceptor and the distances between them in the lattice. The donors are relatively flat brick-shaped molecules. The various configurations with which the bricks are oriented with respect to each other within the lattice determine the dimensionality of the material in terms of electronic conductivity. The $\pi$-orbitals protruding from the donors overlap when these bricks meet approximately face-to-face, producing electronic bandwidth along only one crystal axis. These materials with conducting chains are quasi-one-dimensional (Q1D) whereas a
plane of donors with overlapping orbitals creates a system described as quasi-two-dimensional (Q2D) due to the conducting layers. [3,4]

\[ \alpha-(\text{BEDT-TTF})_2\text{KHg(SCN)}_4 \] provides a complex, but very interesting example of how the arrangement of donors and acceptors often create intricate lattices through which fundamental questions of solid state physics can be explored. The donor molecule, BEDT-TTF (bis(ethylenedithio)tetrathiafulvane), or ET, is shown in Figure 1.1.1a. This combination of carbon and sulfur atoms creates a flat, symmetric structure. The donors are stacked into conducting planes in a configuration called alpha (\( \alpha \)), which precedes the chemical name of the material (Fig. 1.1.1b). The conducting layers are separated by anion planes of \( \text{KHg(SCN)}_4 \) to produce the material, \( \alpha-(\text{BEDT-TTF})_2\text{KHg(SCN)}_4 \). The Fermi surface of this system (Fig. 1.1.1c) contains both flat planes and pockets, thereby showing behavior of a one and two-dimensional material. At low temperatures, changes in transport suggest the formation of a
charge density wave, which is typical of a Q1D material. Quantum oscillations are also observed, resulting from closed electron orbits (Q2D behavior) [5]. Transport and magnetization measurements of the Fermi surface topology explained how this unusual combination of behaviors could occur.

This dissertation describes the systematic studies of two very different organic compounds. The first is a Q2D material in which the donors are configured in a phase known as “tau” ($\tau$). The donor molecules create a square grid in the $ab$-plane which makes up conducting layers. Several tau-phase materials have been investigated with variations in the asymmetric donor molecules as well as the anions. The lattice contains an unique $2:(1+y)$ ratio of cations to anions, resulting in a very complex unit cell. Resistivity behavior typical of Q2D materials is observed in lower applied magnetic fields followed by a metal-to-insulator transition towards the high field limit. Measurements of the pressure and angular dependence of magnetoresistance, magnetization, and skin depth were made for a better understanding of this phase transition.

The second material studied conducts along the stacks of perylene donors which create the crystallographic $b$-axis. Highly one-dimensional materials like (Per)$_2$M(mnt)$_2$ are susceptible to lattice distortions at low temperatures resulting in a periodic electron localization known as a charge density wave (CDW). A competition between the lowered energy of this insulating state and an increase in energy from an applied magnetic field results in a suppression of the CDW. Varying a single site of the anions for these materials from M = Au to Pt, results in greatly varying ground states in high magnetic fields. The application of pressure for the M = Au material results in a suppression of the CDW state from warping of the 1D Fermi surface where quantum oscillations have been observed at higher pressures. The CDW state of the M = Pt compound is destroyed by increasing the field to $\sim$ 20 tesla but a field-induced density wave state develops shortly near 24 tesla. This unconventional high field state is described in chapter 5. These materials were first synthesized almost thirty years ago. Consequently, a significant amount of experimental work has already been done. This research is reviewed in Section 1.3.

1.2 Tau-phase 2D Organic Conductors

The crystal structure of the Q2D tau-phase system is unique in several ways. The donor molecules are asymmetric and contain atomic sites of nitrogen which are not often used in
conventional donor molecules. Although most organic systems are created with a ratio of 2:1 for donors to anions, the anion concentration in the tau systems is not known with certainty. These variations in the donors and anions create a large, complex unit cell. Tight-binding calculations place the Fermi level very close to the edge of a conduction band with a very flat bottom, which may provide a mechanism for magnetic ordering [6].

The pyrazino (P-type) of the DMEDT-TTF (dimethylethlenedithio-tetrathiafulvane) donor is shown in Figure 1.2.1a. The ethylenedioxy (EDO)-type donors (Fig. 1.2.1b) differ from the pyrazino in that the nitrogen atoms are replaced with oxygen. The nitrogen sites in the ring are double-bonded while oxygen sites have single bonds which permits twisting in that ring. The donors are synthesized to have the methyl groups above or below the plane of the molecule, as shown in Figure 1.2.1. Crystals are also synthesized with the reverse orientation. A third type of material is produced where the two types mentioned are randomly distributed in the crystal lattice. The AuBr$_2$ (or AuI$_2$) anions in the tau materials are linear with the gold atom at the center. The first system studied was $\tau$-(P-(S,S)-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, where $y$ was assumed to be $\sim$ 0.75 and (S,S) specifies which isomer (methyl group configuration) is present.

![Figure 1.2.1. The (a) pyrazino and (b) EDO types of the DMEDT-TTF donor molecule.](image)

Tight-binding calculations [7,8] predict a Fermi surface with a shape similar to a star, which covers an area of the first Brillouin zone corresponding to an oscillation frequency of about 950 T. Instead, two frequencies of about 500 T and 180 T were found experimentally for the material containing the pyrazino donor. [9] Surprisingly, the EDO compound has a dominant
orbit frequency of ~ 50 T, though the crystal lattice is nearly identical to pyrazino. [10,11] Analysis of the magnetoresistance peaks yield an effective mass of ~ 7m_e for the highest frequency in the pyrazino compound. Also, the residual resistivity ratio (RRR), calculated from \[\frac{R(T = 300K) - R(T = 4.2K)}{R(T = 4.2K)}\], was found to be negative where a value closer to 100 is expected from a material showing metallic behavior. The large effective mass and unusual RRR provide evidence that the pyrazino tau materials are not strongly metallic. These fermiology studies were carried out in lower field superconducting and dc magnets, which motivated further experiments in higher fields.

Samples cooled to low temperatures and then warmed again exhibited hysteresis in the temperature dependence. Additionally, a large hysteresis was also observed in the low field negative magnetoresistance which precedes the metallic state in which the Shubnikov de Haas oscillations were measured. The symmetric \(ab\)-plane of a pyrazino sample was found to exhibit two-fold or sometimes four-fold symmetry depending on temperature as a sample was rotated with the \(ab\)-plane parallel to an applied constant magnetic field [12,13]. The same measurement for an EDO sample showed a hysteresis with rotation. This was compared to the so-called “magnetic viscosity” observed in \(\kappa\)-(ET)\(_2\)Cu[N(CN)\(_2\)]Cl, which was attributed to a soft lattice [14,15]. This ET system also had a high sensitivity to applied pressure, which will be further discussed in chapter 4.

Nuclear magnetic resonance was studied for the pyrazino and EDO systems, [16] investigating the spin echo signal of the protons. For the pyrazino tau compound, linewidth broadening was observed near 20K along with a peak in the relaxation rate at a slightly lower temperature. Also, specific heat measurements showed a Schottky anomaly at low temperatures which implies a shift between two ground states as temperature was decreased. [17] Both measurements along with the theoretical model of flat-band ferromagnetism provide compelling evidence for the possibility of magnetic ordering in these materials. This will be discussed in conjunction with the high field results in chapter 3 illustrating how an underlying magnetic character may assist in creating the insulating state observed in high fields.

Despite an increase in resistance as samples are cooled to lower temperatures, metallic behavior is observed in the conducting plane when a magnetic field is applied. The Hall effect was measured for pyrazino which gives a carrier concentration of \(\sim 4 \times 10^{20}\) electrons/cm\(^3\) which, for comparison, is two orders of magnitude lower than pure copper [18]. The EDO compound,
with a SdH frequency of 50T, is close to the quantum limit, where the final quantized Landau passes the Fermi level and a gap is opened in the system. If a material has a high enough mobility (i.e. two-dimensional electron gas) then the quantum hall effect (QHE) may be observed if n (the Landau level index) is small enough to allow resolvable peaks in the data. In the EDO compound, Murata et al., [19] observed the $n = 2$ state from the quantum Hall effect near 27 T. A plateau in Hall magnetoresistance was observed in higher fields of $\sim 40 – 50$T. Further, the magnitude of the SdH oscillations for EDO ($\Delta \rho/\rho$) were $\sim 30\%$ [20] where for a pyrazino sample we find a value closer to $1.2\%$. [21] In general, high field magnetoresistance measurements suggest that the EDO compounds are better metals than the pyrazino compounds.

![Figure 1.2.2. The temperature-magnetic field phase diagram for $\tau$-$(P-(I)-DMEDT-TTF)_{2}(A)_{1+y}$ where I is the $(S,S)$, $(R,R)$ or $(r)$ isomer of the donor molecule and A is the AuBr$_2$ or AuI$_2$ anion.](image)

Magnetoresistance measurements of a pyrazino sample in pulsed fields revealed an insulating state in high fields. At temperatures below $\sim 20$K, the conduction electrons become fully localized in fields above 35 tesla. This experiment was repeated for a variety of samples (pyrazino, $(R,R)$ and $(r)$ isomer, AuI$_2$ anion) yielding similar results with each attempt. The phase
diagram for temperature versus magnetic field is shown in Figure 1.2.2, as measured by transport, skin depth and the magnetocaloric effect. All measurements agree that a rapidly widening hysteresis occurs at low temperatures. Measurements of angular dependence revealed that the materials did not follow any type of previously seen field-induced density wave behavior, which are often only seen in Q1D materials. Pressure dependence showed that the insulating state is easily suppressed in both pulsed and dc field by values of pressure as low as 0.1 kbar. Using the results reported in this dissertation, comparisons with isostructural members of the tau-type family, and the background work outlined above, we discuss a working theory of the phase transition in chapter four.

1.3 (Per)$_2$M(mnt)$_2$ where M = Au, Pt

The perylene materials are produced by stacks of the perylene donors molecules and M(mnt)$_2$ (M = metal and mnt = maleonitriledithiolate) molecules along the crystallographic $b$-axis. The $\pi$-orbital overlap from the twenty carbon atoms of each donor creates the conduction paths for the carriers. The lack of transverse bandwidth between the cation and anion chains produces a system which is approximately ten times more one-dimensional than the well-studied Bechaard salts (TMTSF)$_2$X mentioned above. Materials which are strongly Q1D have a tendency towards structural instabilities at low temperature which then lead to charge and spin order.

The first Perylene systems (M = Cu, Ni, Pd) were synthesized in the mid-1970’s [22]. During the following decade, single crystals of M = Au and Pt were produced and found to be metallic to low temperatures [23,24]. These two specific compounds offered several exciting opportunities to experimentalists: 1) to study charge transport in a highly anisotropic Q1D system 2) to compare the effects of spin on conducting chains with an identical material with no spin and 3) to make significant, measurable changes to the crystal lattice using the application of a magnetic field or pressure.

The following sections comprise a brief overview of the research that has been conducted for these materials, lessons learned about the electronic behavior of these materials, and why further experiment are necessary.
Electron paramagnetic resonance was studied for both the M = Au and Pt materials [25,26]. For the S = 0, M = Au system, the g-factor was almost constant over the entire temperature range with almost no linewidth broadening (~0.30 Gauss). A width several hundred times larger was measured for M = Pt, which is related to the spin lattice relaxation rate. The broad linewidth indicates a strong exchange interaction between the conduction electrons and spin chains. The linewidth decreased during cooling to a minimum near 10K, where it then rapidly increases. At the same temperature, the intensity of the EPR signal quickly decreases.

[28] The g-factor for this material comes from an averaging formula where \( g_p \) (\( g_m \)) and \( \chi_p \) (\( \chi_m \)) are the g-factor and susceptibility representing the Perylene (diothiolate) chains, respectively.

\[
g = \frac{g_p \chi_p g_m \chi_m}{\chi_p \chi_m}
\]  
(Eq. 1.3.1)

Proton nuclear magnetic resonance experiments were conducted studying the M = Au and Pt systems [25]. The relaxation rate for M = Pt was almost constant as the temperature was lowered temperatures to ~ 40K where it then decreased monotonically to the base temperature. In contrast, the M = Au sample showed a nearly linear decrease in the relaxation rate through the entire range of temperature. The differences in behaviors is accounted for by considering a sum of separate contributions from dipolar and contact interactions both inter and intra chain. In the
case of M = Pt, it was assumed that the protons, which lie on the periphery of the donor, interact with the spin chain while the M = Au shows more typical, metal-like Korringa behavior. The orbital overlap coming from the carbon sites of the donor are the pathways for the electrons so proposed future NMR experiments will focus on either $^{13}$C or $^{195}$Pt to truly probe the conduction (spin) sites and therefore the interaction between them.

X-ray diffraction experiments have been used to investigate changes in the crystal lattice of $(\text{Per})_2\text{Pt(mnt)}_2$ as the temperature was lowered. Precursor effects are seen as changes in the Bragg reflection as temperatures approached $\sim 3T_c$ where for $M = \text{Pt}$, $T_c = 8 \text{ K}$ [28]. The temperature can be lowered past the transition temperature of $M = \text{Pd, Ni}$ ($T_c \sim 28, 25 \text{ K}$, respectively) to the minimum temperature of the apparatus, which is near 12K. Due to these experimental limitations, achieving a temperature lower than the MI transition is not possible for $M = \text{Pt}$. In the $S = \frac{1}{2}$ chains, dimerization occurs along the spin stacks at the same temperature as the Peierls transition in the conducting chains. Structural x-ray studies for $M = \text{Au}$ have proven inconclusive. It was suggested in past experiments that this material did not go through the same transition as $M = \text{Pt and Pd}$. Later measurements of the current-voltage characteristics of $M = \text{Au}$ at 4.2 K (below the $M = \text{Au}$ transition temperature $\sim 12 \text{ K}$) confirmed the transition to the CDW state. [29]

The susceptibility in the perylene systems contains contributions from the conduction electrons and from the spin chains (in the cases of non-zero spin). At higher temperatures, the paramagnetic susceptibility of the materials with diamagnetic $S = 0$ chains (i.e. $M = \text{Au}$) is larger than expected due to Stoner enhancement. The susceptibility is solely from conduction electrons so it rapidly decreases towards zero at the transition temperature as the electrons became localized [25,30,31]. In measurements of materials containing $S = \frac{1}{2}$ anion chains, the susceptibility was much larger than the $S = 0$ analogs. The unpaired electrons of the spin sites dominate the susceptibility term, making the conduction electron term almost negligible. From room temperature to $\sim 30 \text{ K}$, the susceptibility follows approximately Curie-Weiss behavior. At lower temperatures the slope slowly decreases followed by a peak and a rapid decrease towards zero. The overall behavior of the susceptibility can be approximately fit with the Bonner-Fisher model which indicates anti-ferromagnetic coupling and produces a coupling constant of $J \sim 15 \text{ K}$. The susceptibility does not vary with the applied field aligned or perpendicular to the chains, demonstrating the transition is actually spin-Peierls. For all perylene systems, it is clear that the
anion chains dimerize directly following the tertamerization of conducting chain. The transport properties appear to be independent of the spin chain yet, the Peierls (donor chain) and spin-Peierls (anion chain) transitions occur at the same temperature.

A measurement of thermopower decreased linearly from room temperature to 150K, following metallic behavior. [30] A slope of almost zero followed to 40K when the thermopower for both M = Au and Pt dropped sharply. (Per)$_2$Pd(mnt)$_2$, a very similar system to M = Pt (S = ½), shows a sharp increase in thermopower near the metal to insulator transition. Why the behavior for the M = Au and Pt systems differs from other perylene materials remains unclear. A band filling of ¾ was observed where the filling factor agrees with the bandwidth found by tight binding calculations. The bandwidth values for M = Au and Pt were found to be ~ 0.83 and 0.58 eV, respectively.

Magnetoresistance measurements were first used to probe the CDW state of TTF-TCNQ [32], which has a transition temperature of 53 K. Magnetic fields of 5 tesla were applied but small changes in the magnetoresistance behavior made analysis for the field dependence of the CDW difficult. Almost two decades later, the low CDW transition temperatures of M = Au and M = Pt and improved magnet technology offered a new opportunity to observe a partial suppression of a CDW from an applied magnetic field. Bonfait et al. first performed measurements of magnetoresistance in high magnetic fields on the perylene materials [33], inducing a reduction in the CDW transition of ~ 10% (5%) for M = Pt (Au) at B = 8 T. Further experiments in fields to 18 tesla [34] revealed a further reduction in transition temperature as well as a dependence on the orientation of the applied field to the conducting chains. These initial measurements provided the impetus to probe more deeply into the field-induced metallic states of these materials using the dc high field magnets at the NHMFL.

Magnetotransport measurements studying temperature, angle and pressure dependence were carried out for the M = Au and Pt materials. For M = Au, the suppression of the CDW state closely followed lower field results for other low-dimensional materials. This system regains metallic character in fields beyond 36 T when the magnetic field is aligned with the conducting chain (the phase diagram is given in figure 1.3.2a). The behavior of the shift in transition temperature follows theoretical predictions which suggested the energy gap is similar to a BCS gap and that an applied field will reduce the transition temperature accordingly. The same measurements for the M = Pt compound followed the expected behavior at the lower fields of the
measured range. In the $B \parallel c$-axis orientation in fields of ~ 24 tesla, the conventional CDW state was suppressed. With a further increase in the applied magnetic field the resistance falls several orders of magnitude and a brief metallic state develops. As the field is increased further field-induced insulating state develops, centered around 35 tesla. The resistance decreases again to a strongly activated state in the high field limit (see Figure 1.3.2b). The measurements presented in more detail in chapter 5 suggest this is a field-induced density wave state.

The dissertation sections following this introduction chapter will be organized as follows: the following section provides a theoretical overview of the fundamental physics behind the observations described in the subsequent sections. The third section explains several of the experimental techniques used during these studies. The fourth and fifth sections contain results from the measurements of the tau-phase and Perylene systems, respectively. The final section provides a summary of conclusions and implications for future research.
Figure 1.3.2. Temperature-magnetic field phase diagrams for (a) (Per)$_2$Au(mnt)$_2$ and (b) (Per)$_2$Pt(mnt)$_2$ for the $B//c$-axis orientation. Panel (a) also shows the normalized change in the measured energy gap. The dotted line is used to fit the $B//b$-axis orientation to $\sim B^2$ behavior.

Table 1.3.1. Abbreviated notation for the materials studied.

<table>
<thead>
<tr>
<th>Chemical name:</th>
<th>Notation:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau$-(P-(S,S)-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_y$</td>
<td>$\tau$-AuBr$_2$</td>
</tr>
<tr>
<td>$\tau$-(EDO-(S,S)-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_y$</td>
<td>$\tau$-EDO</td>
</tr>
<tr>
<td>$\tau$-(P-(r)-DMEDT-TTF)$_2$(AuBr$_2$)(AuBr$_2$)$_y$</td>
<td>$\tau(r)$-AuBr$_2$</td>
</tr>
<tr>
<td>$\tau$-(P-(S,S)-DMEDT-TTF)$_2$(AuI$_2$)(AuI$_2$)$_y$</td>
<td>$\tau$-AuI$_2$</td>
</tr>
<tr>
<td>(Per)$_2$Au(mnt)$_2$</td>
<td>M = Au</td>
</tr>
<tr>
<td>(Per)$_2$Pt(mnt)$_2$</td>
<td>M = Pt</td>
</tr>
</tbody>
</table>

It is important to make several comments regarding notation and language used in the text. There are a number of tau-phase structures that were studied as well as two different perylene compounds. The stochiometry of these materials is noted in Table 1.1 with the shorthand notation which will be used to identify them. Also, crystallographic axes will be
italicized in the text (e.g. the crystallographic \textit{a-axis}) for clarity. The terms upsweep and downsweep refer to an increase or decrease in the applied magnetic field, respectively. Frequently in the experiments performed the orientation between crystal axes and the field is important. Expressions such as “the B // \textit{b} orientation” will be used to mean the magnetic field is parallel to the \textit{b}-axis of the crystal lattice.
CHAPTER 2
THEORETICAL BACKGROUND

2.1 – Band Structure and Fermiology

For a better understanding of the ease with which charge can move through a lattice, calculations are carried out to determine the band structure. The tight binding approximation uses a Hamiltonian including a term for a single atom \( H_{atom} \) and terms for the current location of the electron and the rest of the crystal \( (V_o \text{ and } V, \text{ respectively}) \).

\[
H = H_{atom} + \{V(\vec{r}) - V_o(\vec{r})\}
\]  

(Eq. 2.1.1)

Equation 2.1.2a shows the translational periodicity of the Bloch states which are made up of linear combination of plane waves and the atomic wavefunctions, \( \phi \) (Eq. 2.1.2b).

\[
\psi_k (\vec{r} + \vec{T}) = e^{i\vec{k} \cdot \vec{r}} \psi_k (\vec{r}) \quad \text{and} \quad \psi_k (\vec{r}) = \sum_{\vec{T}} e^{i\vec{k} \cdot \vec{T}} \phi(\vec{r} - \vec{T})
\]  

(Eq. 2.1.2a and b)

When the Hamiltonian operates on the eigenstates (Bloch wavefunctions) we have the equations,

\[
\int \phi^* (r) H_{atom} \sum_T e^{i\vec{k} \cdot \vec{T}} \phi(\vec{r} - \vec{T}) d^3 r + \int \phi^* (r) \{V (r) - V_o (r)\} \sum_T e^{i\vec{k} \cdot \vec{T}} \phi(\vec{r} - \vec{T}) d^3 r =
\]

\[
\int \phi^* (r) E(k) \sum_T e^{i\vec{k} \cdot \vec{T}} \phi(\vec{r} - \vec{T}) d^3 r
\]  

(Eq. 2.1.3)

The first and third integrals of Eq. 2.1.3 result are only considered short range (near \( \vec{T} = 0 \)), resulting in constant energies we will label as \( E_\phi \) and \( \beta \), respectively. The second integral is evaluated taking into account the translational lattice vectors, \( \vec{T} = 0 \) and \( \vec{T} = \pm a \hat{\epsilon}_1 \pm b \hat{\epsilon}_2 \pm c \hat{\epsilon}_3 \), where \( \epsilon_1, \epsilon_2, \) and \( \epsilon_3 \) are the primitive lattice vectors and \( a, b, \) and \( c \) are the unit cell parameters. The electrons are assumed to be strongly bound to local sites and the summation only involves nearest neighbors hence the name, tight binding approximation. The overall resulting energy function is

\[
E(k) = E_\phi - \beta - 2t_x \cos(k_x a) - 2t_y \cos(k_y b) - 2t_z \cos(k_z c)
\]  

(Eq. 2.1.4)

where \( t \) is a transfer integral in either the x, y or z direction. [35] The results of this type of calculation can yield an estimate of the electronic anisotropy of a system and the bandwidth of the dispersion in specific crystallographic directions. In organic solids, band structure results can
be found from calculations similar to this simple example. Lattice parameters are determined by x-ray diffraction measurements and input into a tight binding calculations which often provide reasonable estimates for comparison with experiments.

As an electron travels through a lattice it experiences repulsive forces from like charges, attractive forces from screened ionic sites and disorder created by impurities. The effective mass provides a measure of the sum of these forces by indicating if the electron travels easily (light mass) or with difficulty (heavy mass). Newton’s second law \( F = m^* \frac{dp}{dt} \) for the electron and the relation between real and k-space momentum \( \hbar k = p \), lead to the effective mass,

\[
m^* = \hbar^2 \left( \frac{d^2 E}{dk^2} \right)^{-1}
\]

(Eq. 2.1.5)

which is dependent on the curvature of the dispersion relation. As noted above, this will change depending on which crystallographic axis is being observed. [36] This has obvious consequences for one- or two-dimensional organic systems like the ones discussed in chapters 4 and 5.

In the presence of a magnetic field, the path of electron motion is bent from a straight line due to the Lorentz force, \( \vec{F} = q(\vec{v} \times \vec{B}) \) (where \( q \) is the charge, \( \vec{v} \) is the electron velocity and \( \vec{B} \) is the magnetic field). This is easily observed in the Hall effect as a transverse voltage is measured both perpendicular to an applied current and magnetic field. With the application of a field, the momentum of an electron must be replaced by the Landau gauge in the Hamiltonian which includes a term for the vector potential, \( \vec{p} \rightarrow \vec{p} + e\vec{A} \). In addition, the term \( e^{-i\hbar H/\hbar} \) is added to the wavepacket. This satisfies the condition, \( e^{-i\hbar H/\hbar} = 1 \), which ensures that a wavepacket will not destructively interfere with itself but rather create a standing wave. [37] This requires that after time \( \tau \) that \( H \tau = 2\pi\hbar j \), leading to the Bohr-Sommerfeld quantization condition [38],

\[
\oint (\hbar k - e\vec{A})dR = (j + \gamma)2\pi\hbar,
\]

(Eq. 2.1.6)

where \( j = \) integer and \( \gamma = \frac{1}{2} \). Carrying out the integral, the area of the \( j = 1 \) electron orbit in k-space, \( A_k \), is found from the Onsager relation [39],

\[
A_k = \frac{2\pi eB}{\hbar}.
\]

(Eq. 2.1.7)

The area measured is from the Fermi surface, which is the boundary in k-space which separates the occupied wavevector region from the unoccupied region at \( T = 0 \). This boundary
becomes less well-defined with increasing temperature which is why low temperatures are required to observe quantum oscillations. The resulting quantized energy levels of
\[ E = \left(n + \frac{1}{2}\right)\hbar \omega_c \]
are referred to as Landau levels. As the field is increased the area of the orbit also increases. As the area of the orbit nears, passes and then exceeds the area defined by the Fermi wavevector \( A = \pi k_F^2 \), electrons fall to the next quantum level. The oscillating of the free energy of the system is what causes the changes in magnetoresistance (Shubnikov de Haas effect) and magnetization (de Haas van Alphen) which are measured.

The Lifshitz-Kosevich formula (Eq. 2.1.8) [38] below takes into account that measurements are not actually conducted at \( T = 0 \) K and therefore we observe effects which attenuate the oscillations. For a three-dimensional system,
\[
M \propto \left( \frac{B}{\partial^2 a_F / \partial K^2} \right)^{1/2} \sum_{r=1}^{\infty} \frac{(-1)^r}{r^2} \frac{R_D}{\pi} \frac{R_T}{\pi} \frac{R_S}{\pi} \sin[2\pi r (\frac{F}{B} - \gamma) \pm \frac{\pi}{4}] \quad \text{(Eq. 2.1.8)}
\]
where the important factors to take into account are the damping parameters, \( R_T \), \( R_D \), and \( R_S \) (\( F \) is the oscillation frequency). We also see that the oscillations will be inversely proportional to the curvature of the FS \( (\partial^2 a_F / \partial K^2) \). First, \( R_T \) (Eq. 2.1.9) is a measure of the range of orbit frequencies in a system because of temperature variations. The amplitude of any \( n \) peak (e.g. quantum level \( n = 4 \) at 25 T) will increase as the temperature decreases (this is also true of the amplitude of peaks observed in the FFT spectrum). The amplitude of the peaks can then be fit to provide an estimate of the effective mass using equation 2.1.9,
\[
R_T = \frac{\alpha m_e T / B}{\sinh(\alpha m_e T / B)}
\quad \text{(Eq. 2.1.9)}
\]
where \( \alpha = 2\pi^2 k_B m_e / \hbar = 14.69 T / K \) and \( m_e \) is the effective cyclotron mass. The Dingle fitting parameter, \( R_D \), (Eq. 2.1.10) accounts for electron scattering. The oscillation amplitudes will also increase as the field increases following \( R_D \). Using the estimate of the effective mass found from \( R_T \), we then use the Dingle fitting parameter,
\[
R_D = \exp(-\alpha m_e T_D / B)
\quad \text{(Eq. 2.1.10)}
\]
\[
T_D = \hbar / 2\pi k_B \tau
\quad \text{(Eq. 2.1.11)}
\]
to obtain an approximation of the Dingle temperature and then, the relaxation time of electrons in the material. Further, we can find the Fermi velocity, $v_F$, using the relation $v_F = \frac{\hbar k_F}{m_e}$ and the mean free path of the electrons from,

$$l = v_F \tau$$  \hspace{1cm} (Eq. 2.1.12)

A good metal, for example, copper, has a mean free path of \(~33\ \mu m\) by this sort of estimate. The mean free path for the tau materials is found to be as short as \(\sim 150\ \AA\), suggesting excessive scattering and poor metallic character.

A perfectly one-dimensional Fermi surface is flat with no method of producing oscillations of electronic motion. Instead, we again write the Lorentz force in the following manner,

$$\frac{\hbar}{i} \frac{d\vec{k}}{dt} = -e\vec{v} \times \vec{B}$$  \hspace{1cm} (Eq. 2.1.13)

where the direction of motion is along the most conducting direction of a Q1D material (i.e. the $b$-axis of the perylene materials). When a Q1D Fermi surface is warped, or becomes slightly two-dimensional, then oscillations occur as the electronic motion is confined to the non-flat Fermi surface. For example, in a case where current is applied in the $b$-direction ($\vec{v}_b = v_b\hat{y}$) and the field applied along the $c$-axis ($\vec{B} = B_o\hat{z}$), we find that the velocity in $k$-space is the $a$-direction.

The frequency of the oscillations is found from the $k$-space velocity, which determines how often the electron traverses Brillouin zones,

$$\omega_a = \frac{\partial k_a}{\partial t} = \frac{e v_F H_a}{\hbar c}. \hspace{1cm} (Eq. 2.1.14)$$

As the real space velocity is always perpendicular to the Fermi surface when a 1D surface is warped, the velocity “waves” back and forth. This cannot be measured in the same manner as the closed orbit oscillations described above and instead requires spectroscopic techniques.
2.2 – Instabilities of Quasi-One-Dimensional Systems

2.2.1 – The Peierls Transition

The strongly anisotropic materials discussed in chapter 5, have a ratio of intrachain to interchain conductivity which has been measured to be ~ 900 [40]. A perfectly one-dimensional system would be impossible to synthesize but the perylene-based organics provide a close approximation. Peierls first proposed a low temperature lattice distortion based on a one-dimensional chain of atoms [41]. A 1D electron gas is actually unstable against any lattice distortion, shifting every second, third or n\textsuperscript{th} atom, because a distortion can always be found (theoretically) which lowers the electronic energy by opening a gap at the Fermi level. The decrease in the energy of the electrons must compensate for the cost in energy of moving lattice sites closer together. The Peierls distortion sometimes results in periodic localization of the electrons called a charge density wave (CDW). First, the response of the electron gas under this condition with be mathematically introduced followed by a qualitative example which explains the net result.

The Lindhard response function, $\chi(q)$, shows the reaction of the free electron density, $\rho(q)$, to the periodic potential, $V_q$.

$$\rho(q) = -V_q \chi(q)$$

(Eq. 2.2.1)

The function in one-dimension is given by,

$$\chi(q) = -\frac{e^2}{\pi\hbar v_F} \ln \left| \frac{q + 2k_F}{q - 2k_F} \right|.$$ 

(Eq. 2.2.2)

and is shown in Figure 2.1.1, where it diverges at $2k_F$. The result of this response is a periodic density of the charge which may or may not be commensurate with the spacing of the lattice.[42]
An idealized case is used to aide the explanation. A perfectly 1D lattice of nearly free electrons with a half-filled band (lighter grey shading of Fig. 2.2.2) and with lattice spacing \( a \) and will have a dispersion relation based on the kinetic energy of the electrons,

\[ \varepsilon(k) = -2t_x \cos(k_x a). \]  

(Eq. 2.2.3)

The boundaries of the first Brillouin zone and the Fermi wavevector will be located at \( \pm \pi / a \) and \( \pm \pi / 2a \), respectively. If the chain becomes distorted so the lattice spacing is doubled to \( 2a \) (the lattice sites become dimers), the Brillouin zone is halved. A gap is opened at the new zone boundary. The same result is expected in the case of the perylene systems which have \( \frac{3}{4} \)-filled bands resulting from hole transport. In this case the donor molecules are tetramerized during the Peierls transition rather than forming pairs. The overall energy of the system is lowered (darker grey filling in Fig. 2.2.2) because the Fermi level lowers with the opening of the gap (\( \Delta \)).

Experimentally, the opening of the gap in observed in measurements as an increase in sample resistance as the temperature decreases. The resistance behaves as,

\[ R(T) = R_0 e^{-\Delta / k_B T}. \]  

(Eq. 2.2.4)

where \( k_B \) is Boltzmann’s constant. When the natural log of the resistance is plotted versus the inverse of the temperature (an Arrhenius plot) a line fit gives an estimate of the gap value.

Figure 2.2.2. Peierls distortion of a half-filled band for a system with lattice spacing \( a \). The halving of the first Brillouin zone creates a gap at +/- \( k_F \). Lighter grey indicates the filling to the Fermi level before the distortion and the darker grey indicates the filling after the first Brillouin zone is reduced in half. \( \Delta \) is the energy gap.
2.2.2. The Spin-Peierls Transition

The Pt(mnt)$_2$ chains of (Per)$_2$Pt(mnt)$_2$ begin as typical Heisenberg antiferromagnetic chains with coupling between nearest neighbor S = $\frac{1}{2}$ Pt sites. [43,44] The transition which takes place at low temperatures is easily explained following the previous section regarding the Peierls transition. For a spin-Peierls (SP) transition, the lattice chain dimerizes, which pairs the spins of the chain. This must lower the magnetic energy of the system more than lattice coupling in the system increases. The coupling constant J between neighboring spin sites, becomes two separate constants, $J_1$ and $J_2$ as the lattice spacing changes but the overall exchange energy does not change. A simple example follows from a 1D lattice which has a strong Coulomb interaction among electrons which produces a localization of one electron per site. The electrons and sites will form pairs to lower the magnetic energy. The (Per)$_2$Pt(mnt)$_2$ system, where the Pt sites reside in the center of the anion molecules, goes through a spin-Peierls transition at the same temperature that the conducting chains go through the Peierls transition.

2.2.3. Spin density waves

The spin susceptibility, under the correct conditions, displays ferromagnetic behavior if the Stoner criterion is fulfilled. The requirements are a large density of states and a strong Coulomb repulsion. Even if the conditions are not completely met, it is possible that susceptibility will be enhanced. Another low temperature density wave ground state is possible in 1D systems which have large Coulomb interactions and density of states. This state is periodic with respect to spin rather than charge.

A CDW is produced by electron-phonon interactions whereas a spin density wave (SDW) is created by interactions between electrons. The lattice is not distorted for this state, therefore the transition to a SDW is not detectable by the techniques used to probe the structure of CDW systems (i.e. x-ray diffraction and neutron scattering). [45] Similar to the response function calculated for the charge modulation of the crystal the spin susceptibility is subject to a wavevector-dependent enhancement which is unstable for $q = 2k_F$. [46] With this susceptibility, electrons become localized near the lattice sites and the overall energy of the system is lowered by a gap opening at $\pm \frac{\pi}{a}$, where a is the lattice spacing. A SDW is most easily thought of as
two CDWs, one of spin up electrons and the other with spin down. The two waves are out of phase by $\pi$, and the expected lattice distortions cancel each other out. [44]

### 2.2.4 – An aside: Field-Induced Spin Density Waves

All of the instabilities mentioned above require a material to be electronically one-dimensional. In a perfect 1D material, electrons are scattered with phonons of wavevector $Q = 2k_F$, back and forth in an “umklapp scattering process” between the FS sheets. In a quasi-1D material, the Fermi surface becomes warped but parallel section of FS sheets are still possible. The wavevector is slightly more complicated as $Q = 2k_F \hat{x} + \frac{\pi}{b} \hat{y}$ where $b$ is the lattice spacing in the second most conducting direction. A vector such as $Q$ is called the nesting vector and maps out the overlap from 1D (or Q1D) sheets, were $2k_F$ scattering processes can occur. This effectively makes the material more 1D and prone to the instabilities previously described. As further warping occurs for the Fermi surface, perfect nesting becomes more difficult and eventually small pockets are formed between the mismatched Fermi surface sheets.

The SDW is of great interest in the discussion of low-dimensional organic systems, because it is the low temperature ground state of the Bechgaard salts, $(TMTSF)_2X$, which have been mentioned previously. For the Bechgaard salts, the conductivity along the axes from greatest to lowest is $a$, $b$ and then $c$-axis. Without a lattice distortion for the SDW, typical detection techniques for a CDW cannot be used (ie. x-ray diffraction) but instead electron spin resonance (ESR) or nuclear magnetic resonance (NMR) may be used due to the coupling of the lattice with the spin waves. In the specific case of $X = \text{ClO}_4$, slow cooling orders the anions of...
the lattice, which causes a dimer along the \( b \)-axis. This causes a doubling of the unit cell (real space) which causes a halving of the first Brillouin zone (k space), along the \( k_a \) direction with now four warped Fermi sheets, rather than two. Spin density wave formation is not, of course, strictly confined to organics but we will discuss the field effects on a SDW for the Bechgaard charge transfer salts, as they are the most famous and well-studied case.

The one-dimensional systems of chapter 5, \((\text{Per})_2\text{M(mnt)}_2\), do not go through a SDW transition at low temperatures. This has been confirmed with x-ray diffraction studies which clearly show differences in the crystal lattice above and below the transition temperature. The comparison of interest between the TMTSF and perylene based systems, in under the influence of strong magnetic fields. The anisotropy between first and second most conducting axes is approximately ten times stronger for the perylene systems. This means there is less warping for the Fermi surface of the Perylene systems and nesting (i.e. Q1D character) is more easily achieved.

Pockets are formed between imperfectly nested, warped FS sheets. When the field is turned on, Landau levels (LL) are formed. [47] The Fermi level falls into the gap between successive LL and a SDW state forms. The nesting wavevector is modified to produce this condition,

\[
\vec{Q} = (2k_F \pm \frac{n2\pi}{\lambda})\hat{x} + (\sim \frac{\pi}{b})\hat{y}
\]

(Eq. 2.2.5)

where \( n \) is an integer, \( H \) is the field strength, and \( b \) is the lattice spacing (replaced by \( a \), in the case of perylene systems). In the second term in the \( \hat{x} \) component \( \lambda \) is the magnetic length which is the distance in real space between peaks of electron motion along the \( a \)-axis. Because the overall energy of the system is lowered by sustaining this state, as the field is lowered the wavevector will reposition to maintain the Fermi energy between Landau levels. This leaves a gapped state where the lower Landau band is completely filled and the one above is completely empty. A quantized nesting model was developed to describe the FISDW state [48]. In an ideal case using this model one would experimentally observe an increase in magnetoresistance at each point in an increasing field where the Fermi level becomes fully gapped. Because it originates from the quantized energy levels, the cascade of FISDW states should be periodic with inverse magnetic field.
Increasing the strength of the magnetic field decreases the magnetic length and increases the confinement of the electrons to the chains. One-dimensionality is also increased as the magnetic energy becomes larger than the thermal energy which allows hopping between chains. Further, the magnetic energy also becomes larger than the transverse transfer integral, lowering dimensionality one step further. The salt \((\text{TMTSF})_2\text{ClO}_4\) follows the behavior described in a magnetic field. Low fields first destroy the superconductivity. Increased magnetic fields produce the first gapped, SDW subphase around 2.5 tesla. A cascade of the subphases are observed to \(\sim 8\) tesla when the \(n = 0\) Landau level is reached and the system remained gapped.

2.2.5 – The CDW energy gap: Low Temperature and Field Dependence

The gap which opens during the Peierls transition was compared to a BCS (Bardeen-Cooper-Schrieffer) energy gap by Rice and Strassler [49]. Both transitions rely on a phonon-electron interaction to mediate the low temperature ground state. Rice and Strassler, began from the Fr"ohlich Hamiltonian used in the BCS theory and added a term describing the phonon distortion of the Peierls transition. The resulting electron dispersion for electrons is similar to that of the BCS electron pairs. The frequency of the lattice vibrations decreases to zero at the phase boundary at which point the order parameter, \(\Delta\), begins to grow. The results of their analysis show that the gap formation at the transition temperature is also a second order phase transition. The transition temperature was found to be

\[
k_B T_c = 2.28 \varepsilon_F e^{-2b}
\]

(Eq. 2.2.6)

where \(b = \hbar \omega / (2N(0)g^2)\) (\(\omega\) is the phonon frequency, \(\hbar\) is Planck’s constant, \(N(0)\) is the density of states at the Fermi level and \(g^2\) is the response function). The Peierls distortion and BCS superconducting transition have several similarities. [50] First, as with all of the instabilities mentioned for the low-dimensional systems, the formation of a gap decreases the energy of the electrons making the new state favorable. Second, scattering impurities in the Peierls state have the same effect as magnetic impurities in a superconducting state. Third, the zero-temperature gap value is predicted by the transition temperature in both cases by,

\[2\Delta(0) = \xi k_B T_c\]

(Eq. 2.2.7)
where $\Delta(0)$ is the gap value at $T = 0$ and $\zeta$ is $\sim 3.5$ for SC and $5 - 10$ for CDW ground states. [42]

The parallel between the BCS gap and that of the Peierls distortion was extended by Dietrich and Fulde [51] to explain the dependence of the transition temperature on the magnetic field. One of the initial assumptions of the analysis includes that the Fermi level is in the center of the conduction band. The magnetic field in this analysis is understood to only affect the conduction electrons of the system, meaning this treatment does not include the $S = \frac{1}{2}$ Pt sites of the spin chains, but instead focuses solely on the perylene chains. The magnetic field dependence of the shift of the transition temperature is found from the equation,

$$\frac{\Delta T_c}{T_c} = F\left(\frac{E_F}{T_c}\right) \cdot \left(\frac{\mu_B B}{k_B T_c}\right)^2$$

(Eq. 2.2.8)

where $\Delta T_c$ is $T - T_c(B=0)$, $\mu_B$ is the Bohr magneton, $k_B$ is Boltzmann’s constant and $B$ is the applied field. The function $F$ is defined as

$$F(x) = \frac{1}{8\pi^2} \cdot \frac{\text{Re} \psi^\prime\prime \left(\frac{1}{2} + i \frac{x}{\pi}\right) + \psi^\prime \left(\frac{1}{2}\right)}{x \text{Im} \psi^\prime \left(\frac{1}{2} + i \frac{x}{\pi}\right) + 2},$$

(Eq. 2.2.9)

where $\psi$ is the polygamma function (derivation of the digamma function) and the real and imaginary components are taken as shown. $F(x)$ is evaluated with the argument of $E_F/T_c$, where we estimate $E_F$ to be near 5000 K and $T_c$ is near 10 K for both the $M = Au$ and Pt systems. In this limit, where $E_F >> T_c$, the function becomes -0.21.

The work of Tiedje, et. al. [32] provided experimental evidence of the field dependence. The magnetoresistance of TTF-TCNQ, a Q1D system, was measured in fields of 5 T. This material is metallic to 53K, where a gap opens and creates a semi-conductor. Focusing on the same interaction they approximated a magnetic field dependence of the transition temperature by

$$\frac{\Delta T_c}{T_c} = -\frac{\gamma}{4} \left(\frac{\mu_B H}{k_B T_c}\right)^2.$$

(Eq. 2.2.10)
2.2.6. Field-Induced Charge Density Waves

The experiment results discussed in chapter 5 for (Per)$_2$Au(mnt)$_2$ generally follow the predictions of field dependence from the equations above. The CDW ground state is almost undetectable beyond 36 tesla, depending on the orientation between the field and crystal. Unexpected high field behavior was found while measuring (Per)$_2$Pt(mnt)$_2$. With a $T_c$ of only 8K, the insulating state of M = Pt is quickly suppressed in fields as low as 20 tesla. Curiously, more interesting behavior lies above this field where another density wave state forms.

Zanchi, Bjelis, and Montambaux [52], (hereafter, ZBM) give a theoretical description which predicts some of the behavior observed in the Perylene materials. Rather than destroying the CDW by Zeeman splitting (Pauli limit), the high field states are affected by both Pauli and orbital effects. As opposed to conventional theories, CDW and SDW ground states are treated together. While elements of this theory may also apply to the M = Au system, it is easier to correlate expectations with the M = Pt because of the large impact of the magnetic field due to the lower transition temperature of M = Pt.

In ZBM theory the nesting vector, which is static for most low temperature states, shifts with a changing magnetic field. The transition temperature decreases monotonically is lower fields, as expected for a conventional CDW (referred to as CDW$_o$). The impact of the Pauli and orbital terms are defined by $q_p = \frac{\mu_B H}{v_F}$ and $q_o = e b H \cos(\theta)$, respectively and

$$\eta = \frac{q_o}{q_p} = \frac{ebv_F \cos(\theta)}{\mu_B}$$

is the ratio of their strength. The ratio of coupling constants for spin and charge is defined as $\nu = -\frac{U_x}{U_C}$. Depending on the above parameters the wavevector can shift along the conducting chain (CDW$_x$ order) or perpendicular to the chain (CDW$_y$ order). CDW$_x$ depends of the Pauli term exclusively and is a hybrid of CDW and SDW terms. CDW$_y$ depends on interchain coupling and is composed of the SDW components which are perpendicular to the applied field.

The initial conditions assume that the system is perfectly nested using $\vec{Q} = 2k_F \hat{x} + \frac{\pi}{b} \hat{y}$. The wavevectors calculated in this treatment, $\vec{q}$, are deviations from this condition (i.e. the new wavevector = $Q + q$). The shift of the wavevector ($q_x$) along the
conducting chain is brought on by the application of high fields. The transverse shift ($q_y$) depends on solely on $t_b$ (using ZBM notation, this is the transverse hopping integral whereas for the perylene materials, it is $t_a$) and $\eta$, the ratio of the Pauli and orbital parameters. By including the $\eta$ term, we are considering the direction of the field within the transverse plane where $\theta = 0^\circ$ is aligned with the $a$-axis of the perylene materials.

Imperfect nesting in a Q1D system can be experimentally achieved by the application of pressure. The value $t'_y$ is the anti-nesting parameter which is approximated by $t'_y = \frac{t_y^2}{t_x}$, where we use the conduction chain ($t_x$) and transverse ($t_y$) transfer integrals. Using this parameter with $t'_y \ast$ (the value which would suppress the CDW state at $B = 0$, $T_c(t'_y = 0)$) we can measure the degree of imperfect nesting by $\frac{t'_y}{t'_y \ast}$. Using the calculated values for perylene systems we find this ratio is $\sim 0.040$, which is very near to the perfectly nested limit at ambient pressure (see figure 2.2.4). With the addition of pressure, the CDW transition temperature decreases. As the degree of imperfect nesting approaches $\sim 1$ the normalized transition temperature is expected to show cascade-like behavior.

![Figure 2.2.4. Field dependence of normalized transition temperature ($T_c/T_c(B=0)$) in terms of imperfect nesting. The nesting of the Fermi surface is increasing less perfect from top curves to bottom. (This figure was taken from ref. 52, Fig. 9.)](image)

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In an effort to build onto the original FISDW theoretical framework of Gor’kov, Lebed used the same formalism adding a term to include Zeeman effects. [53] Distinguishing features of this theory in comparison with FIDW include a lower expected transition temperature and large shift in FICDW cascade effects at critical angles. The order parameters for this calculation is specifically found to depend on the nesting vector of the system,

$$\Delta_{\text{FICDW}}(r) = \Delta e^{iQr}$$ \hspace{1cm} (Eq. 2.2.11)$$

where

$$\bar{Q} = (2k_F + K)\hat{x} + \frac{\pi}{b^*} \hat{y} + \frac{\pi}{c^*} \hat{z}.$$ \hspace{1cm} (Eq. 2.2.12)

The additional term, $K$, within the $x$-component of the nesting vector is

$$K(H, L) = \pm \frac{2\mu_B H}{v_F} + 2L \frac{\omega_c(H)\cos(\theta)}{v_F}$$ \hspace{1cm} (Eq. 2.2.13)$$

where $L$ is an integer. The frequency corresponding to the electron path along the FS is defined as $\omega_c = eHv_Fb^*/c$. In figure 2.2.5, the transition temperature is proportional to

$$T_{\text{FICDW}} = \frac{He^{\lambda'}}{g_{\text{eff}}(H)}$$ \hspace{1cm} (Eq. 2.2.14)$$

where $H$ is the magnetic field and $g_{\text{eff}}(H)$ is proportional to the maximum value of first and second order Bessel functions squared (Fig. 2.2.5, inset). The field term and exponential above result in a cascade of oscillating transition temperatures in an applied field.

![Figure 2.2.5. The transition temperature of the FICDW is dependent on $g_{\text{eff}}(H)$. $\lambda'$ is proportional to inverse field. (Taken from Ref. 53, Fig. 1) Inset: Dotted line shows maximum value of first (blue) and second (red) order Bessel functions squared.](image-url)
CHAPTER 3
EXPERIMENTAL METHODS

3.1 Sample synthesis, morphology, and quality

High purity samples are critical to reproducible experiments to generate conclusive results. Growing samples is a time consuming and difficult process. It can be disturbed by slight vibrations, and the yield of high quality samples is often low. Not every sample can be checked by x-ray diffraction to determine the parameters of the unit cell so uniformity within a batch of crystals is an important consideration when samples are harvested.

![Sample photos](image)

Figure 3.1.1. Photos taken under a microscope of samples of (a) (Per)$_2$Pt(mnt)$_2$ and (b) (Per)$_2$Au(mnt)$_2$. The sample width indicated by the arrows is approximately 300 and 30 µm for (a) and (b), respectively.

The sample growing process for most organic crystals is broken down into two steps: (1) synthesis of the donors and acceptors molecules and (2) changing the molecules into radicals so single crystals can be formed using electrochemistry techniques [54]. The syntheses techniques used to produce the perylene and tau-phase materials are outlined in Refs. 23 and 55. The quality of samples can be estimated from observations under a microscope. Typically, crystals of good quality are black with a clean, shiny surface. Single crystals are found in a number of shapes. For example, the tau-phase crystals are plate-like with a variety of thicknesses ranging from a few microns to a millimeter. The perylene crystals are needle-shaped and with dimensions that rarely exceed 50 x 100 µm along the shorter two axes, for a single crystal of good quality. These dimensions may be larger for a polycrystalline sample, as shown in Fig. 3.1.1a.
The $M = \text{Au}$ sample shown in Fig. 3.1.1b can be determined to be a single crystal by the uniform manner in which light reflects from its surface, which allows us to assume long range order in the crystal. The $M = \text{Pt}$ sample in Fig. 3.1.1a is actually a cluster of smaller crystals which did not completely separate during the electrocrystalization process. It is obvious that the surface of the sample is not smooth, raising questions about the quality of all of the crystals from this batch.

3.2 Magnetotransport

Many of the results reported in chapters 4 and 5 measure magnetotransport. In this method, thin (~ 12 $\mu$m) gold wires are attached to the sample using either silver or carbon paint. To measure sample resistivity using ac methods, a voltage (~ 1 V) is applied through a resistor (~ 1 M$\Omega$) and the resulting current flows through the sample. The output sample voltage is measured using a Stanford Research Systems (SRS830) lock-in amplifier, which is set to monitor the frequency of the current, usually 10 – 100 Hz. The value of the current is usually chosen considering the factors (a) signal-to-noise ratio, (b) heating and (c) possible degradation of sample/contacts. In some cases, we use a quasi-dc method which uses a Keithley 220 current source, which steps between +/- current for a predetermined time interval. This switching of the current triggers a Keithley 2182A nanovoltmeter which measures the voltage. The ac method is reliable for samples with resistances between ~ 0.100 – 100k Ohms, but often the dc method using higher currents are needed to check results below the range. At very high resistances, and electrometer or other methods must be used for reliable results because the sample resistance equals the resistance of the calibrated resistor which determines the current.

The configuration of the contacts depends on the sample being measured. For example, the resistivity of the Q2D tau-phase crystals are measured interplane along the most resistive axis (the $c$-axis, perpendicular to the conducting layers), as shown in Fig. 3.2.1a. For the Q1D perylene systems we measured along the conducting axis of the crystal (Fig. 3.2.1b), which is easily determined because it is the longest axis of the needle-shaped crystal. The $a$- and $c$-axes of the perylene compounds are not as clear. An x-ray diffraction measurement was performed on an unusually large crystal. [56] The $c$-axis was found to be along the shortest dimension of the
single crystal with the $a$-axis following the width. The results presented in Chapter 5 follow this assumption for each sample measured.

![Diagram](image)

Figure 3.2.1. Contact configuration for transport measurements of the (a) tau-phase and (b) perylene materials. The arrows represent the crystallographic axes of the samples.

### 3.3 AFM cantilever methods

Among the techniques used to probe the Fermi surface of layered materials, one can either measure the oscillating magnetoresistance via the Shubnikov de Haas (SdH) effect or the magnetization through the de Haas van Alphen (dHvA) effect. Because it is a resistance measurement, the SdH signal is strongly dependent on the quality of the sample as impurities can increase scattering and decrease the amplitude of the signal. The measurement also depends on the dimensions of the sample and whether they are large enough for attaching contacts. In high fields, a capacitance cantilever is often used to measure the magnetization of a sample. This technique involves attaching a sample to a small, thin sheet of beryllium copper (BeCu) using vacuum grease (Fig. 3.3.1a). Another sheet of BeCu lies a uniform distance beneath the top sheet. The torque created by the sample magnetization ($\bar{N} \propto \bar{M} \times \bar{B}$) is monitored as a capacitance measurement when distance (d) between the sheets changes. Samples with large magnetic moments or mass can be moved closer to the pivot point between the sheets. One disadvantage to
this technique is that BeCu is a relatively stiff material so samples with smaller masses or weak moments are difficult to detect.

3.3.1. (a) A capacitance cantilever with two BeCu sheets. (b) Schematic of a piezo-resistive AFM cantilever, used for magnetization measurements (drawing not to scale). (c) Cross-section of the sample platform and cantilevers used with a rotation probe. The axis of rotation is into the page, noted by the black “x”.

Recently, commercial piezoresistive cantilevers [57] have been tested in high fields. They can also be used for measurements of quantum oscillations [58,59] and phase transitions with a magnetic signature [60]. The cantilever has two arms of nearly equal resistance one of which is used for mounting the sample while the other serves as a constant reference (labeled R_s and R_r in Fig. 3.3.1b, respectively). Fig. 3.3.2 shows the temperature dependence of the cantilever arms are shown, measured in series. The dimensions of the piezoresistive material of both cantilever arms are identical and contribute equally to the measured resistance (the red arrow of Fig. 3.1.1b shows one point of piezoresistive material). The resistance of the sample and reference arm drop monotonically to ~25K, where the resistance becomes nearly constant. The resistances of these arms are used with two decade boxes (R_1 and R_2) to create a bridge circuit by first connecting all of the resistors in series, as depicted in the inset to Fig. 3.3.2. Of the four gold pads shown in the schematic above (Fig. 3.3.1b), the two middle pads are shorted together, at point A. An excitation voltage of hundreds of millivolts and tens of Hertz is applied across point A to D
(between the decade boxes). The circuit is shown in figure 3.3.2 inset. At low temperatures, where the measurement is conducted, the resistance circuit is balanced by changing the values of the decade boxes until the lock-in amplifier reading is nearly zero.

![Figure 3.3.2 – Cooling curve of the sample and reference arm of the PRC120 cantilever measured in series. Inset: Bridge circuit incorporating the arms of the cantilever (R_S and R_T) with two decade resistance boxes (R_1 and R_2).](image)

Samples are attached to the sample arm of the cantilever using 5-minute epoxy. Silver paint has also been tested for securing the sample but it is more brittle than epoxy when dry. It is also possible to use vacuum grease however, it poses a risk in that the sample can shift position at higher temperatures where the grease is not completely solid and then be frozen into an incorrect orientation when upon cooling. When the sample is mounted using epoxy, a sample is attached with a small amount of vacuum grease to the tip of a micropositioner. A small “bulb” of mixed epoxy is collected at the end of a sharpened wooden application stick. The bulb of epoxy is brought into contact with the sample arm of the cantilever by hand, leaving a small deposit of epoxy at the tip but without making physical contact between the wood and cantilever arm. The sample is then brought into position where it may be reoriented using the micropositioners. The sample is left to cure for 20 minutes. The micropositioner tip and vacuum grease are then slowly
withdrawn from the sample. Additional epoxy can be added using the micropositioner if the cantilever-sample joint does not appear to be stable.

Figure 3.3.3. Cantilever response for $\tau$-(P-($\tau$)-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ at the angular orientations noted in the figure. Inset photo: The tau-phase single crystal mounted to a PRC120 cantilever. The white rectangle covers the sample arm of the cantilever to clearly show the scale of the sample and the device. The drawing shows the $\theta = 90^\circ$ orientation of the cantilever.

The cantilevers offer a sensitivity of $10^{-13} - 10^{-14}$ Am$^2$, [61] which is at least two orders of magnitude better than a commercial dc SQUID [62]. A clear advantage of these cantilevers is the ability to measure the magnetization of very small samples. For example, Ni(tmdt)$_2$, was the first molecular metal synthesized from a single type of organic molecule (ie. not a donor and anion), showing metallic behavior to low temperatures [63]. The dimensions of Ni(tmdt)$_2$ are on the order of 130 x 100 x 20 $\mu$m$^3$, with a mass near 1 $\mu$g. It is too small for an accurate measurement with a capacitance cantilever or to attach contacts to measure magnetoresistance. Instead, the de Haas van Alphen effect was measured using the piezoresistive cantilevers described above to
investigate the Fermi surface of the material as further evidence of a metallic state [64]. The resulting surface matches well with predictions from band structure.

Figure 3.3.4. De Haas van Alphen signal measured at 0.5 K using a nearly cylindrical sample of pure Pb attached to a PRC120 cantilever. Inset: An enlarged view of the low field limit from the same measurement showing the Meissner effect before the superconducting state is destroyed.

The magnetization measured will not correspond directly with the orientation of the cantilever to the magnetic field if the sample is not mounted at the tip of the sample arm, but rather under it or over it, (see the photo inset to Fig. 3.3.3.). For example, the results of the angular dependence from $\tau-(P-(r)-DMEDT-TTF)_{2}(AuBr)_{1+y}$ (Fig. 3.3.3) are not well-understood due to the position of the sample under the sample arm rather than the tip. These effects are amplified when measuring samples near the high mass limit of the cantilever, which has been estimated to be $\sim 0.5$ mg from the fracture of several cantilever sample arms. In these cases, the weight force on the sample competes with the force from the sample magnetization and applied field. This results in angular dependence which is difficult to interpret. If a sample is mounted nearly perfectly at the tip of the sample arm, a flat background signal is observed. In the case of a small, nearly cylindrical sample of high purity Pb, (Fig. 3.3.4, inset) the superconducting transition is observed at low fields from the Meissner effect. As the field is increased, de Haas
van Alphen (dHvA) oscillations are observed (Fig. 3.3.4). The cantilever technique was used to measure the phase transition of both tau and perylene samples. More details associated with these measurements are provided in chapters 4 and 5. Appendix A provides more information about the cantilevers.

### 3.4 High pressure methods

![Figure 3.4.1 Schematic drawing of the components of a BeCu double-clamped pressure cell.](image)

Applying quasi-hydrostatic pressure can change the lattice parameters of a crystal. The effects are even more dramatic for organic materials, which typically have a soft lattice in comparison to inorganics. The Young’s modulus for organic materials is on the order of $10^{10}$ N/m$^2$ or less [65]. In contrast, inorganic materials, using Sr$_2$RuO$_4$ for an example ($\sim 1.8 \times 10^{11}$ N/m$^2$), [66] are several times higher and approach the modulus of the BeCu cell ($10^{11}$ N/m$^2$ or larger). Pressure has become an invaluable tool for exploring the phase diagrams and electronic structure of low-dimensional systems. The first organic superconductor, (TMTSF)$_2$PF$_6$, required $\sim 6$ kbar of pressure to suppress a low temperature spin density wave state before superconductivity could be observed [2]. In general, the addition of pressure increases the dimensionality of a system, which plays a crucial role in measurements of the perylene systems.
To prepare the samples to measure magnetotransport in a pressure cell (Fig. 3.4.1), electrical leads (~12 µm Au wire) are first added to the samples using silver or carbon paste, in the same way as in an ambient pressure measurement. A key difference is that the samples often must be cleaved to fit on the sample stage (piece #6, Fig. 3.4.1) which has a 3 mm diameter. The sample size must be further reduced in the cases where 3-4 samples are mounted on the same stage. The samples are then attached to thin copper wires, which are fixed in place through the stage using Stycast 2850 FT epoxy. Manganin wire (3-5 cm) is sometimes soldered into place on the stage to provide a calibration of the pressure. The resistance of manganin wire has been proven to increase 0.248% with each kilobar of additional pressure. [67] Other methods for calibrating pressure include either measuring the shift in the superconducting transition temperature for Pb or the change in the peak position of the absorption spectrum for a ruby crystal.

The pressure medium used is Daphne oil 7373 [68]. The oil does not react with the silver or carbon paint contacts. Using an InSb pressure gauge, it has been observed that ~ 1.5 kbar of pressure is lost during the entire cooldown from room to low temperatures. This value is independent of the initial pressure at room temperature. The solidification of the Daphne oil begins near ~ 220 K. The cooling process should be slow and carefully monitored as the samples can be damaged during this phase transition. Any pressures mentioned in this dissertation will be the pressure at low temperature ($P_{LT}$), where the magnetoresistance was measured, rather than the pressure at room temperature ($P_{RT}$), where $P_{LT} = P_{RT} - 1.5$ kbar.

The assembly of the pressure cell is described in the following procedure. Note that the BeCu stock is heat-treated at 315 °C for 2.5 hours before providing it to the NHMFL shop for machining. This increases the hardness of the material without causing it to become brittle. First, the Cu wires of the sample stage must pass through a tungsten carbide (WC) feedthrough and the bottom clamp of the cell (pieces 7 and 8, respectively). The Teflon cup (piece 5) is filled with the pressure medium and a thin layer of vacuum grease is applied to the edge cup to guard against leaks. The centering ring (pieces 4) is moved into the bore of the cell as shown in the figure. The sample stage is then wetted with the pressure medium to provide support from underneath to the samples. The sample stage is then introduced into the Teflon cup. Great care must be maintained because the samples and Au wires are easily moved or damaged. The coupled stage/cup is pushed into the bore of the cell body (piece 9). The bottom clamp is then screwed into its final
position using a screwdriver with a “V cut into it to work around the Cu wires. WC pieces 2 and 3 are set into place above the centering ring and the top clamp (piece 1) is added.

The entire assembly is placed in a holder to ensure that the wires will not be damaged and the cell is perpendicular to the laboratory press while adding pressure. A WC piston (~ 4 cm in length) is moved into the bore of the top clamp. The piston and cell are placed between the two parallel plates of the laboratory press where the manganin wire resistance is noted before and after adding pressure. Pieces 2 and 3 are moved downward as the press increases the load on the piston. When a final position (pressure) is reached, the top clamp is turned with a locking wrench. The load of the lab press is then monitored for 10 minutes. If the load decreases, then the cell assembly has an oil leak and must be disassembled and repaired. If the value remains static, the load is gradually decreased and the samples are considered ready to be measured.

Though the addition of pressure is useful for increasing the dimensionality of the sample, the experimental volume available in the bore of the magnets usually does not allow for rotation of the cells. This makes measuring angular dependence impossible. To solve this problem, pressure cell bodies were reduced in length ~ 20% and the clamp holes were retapped to clean the threads. Shorter versions of pieces 3 and 7 were used with a shortened Teflon cup to accommodate this loss of length. The remanufactured cell allowed for rotation in wider bore magnet systems.

3.5 Pulsed magnetic field measurements

The dc fields of the Tallahassee magnet laboratory are created using high currents from a power supply and a water-cooled copper-alloy solenoid. Pulsed magnets create the highest fields but for a period on the order of milliseconds. A power supply is used to create a large voltage across a bank of capacitors. The magnet is submerged in a container of liquid nitrogen to lower the resistance of the magnet and to limit magnet heating during the pulse. The stored potential is then released through the pulse magnet. The magnet, capacitor bank and overall resistance of the system create a LRC circuit. A crowbar diode is placed in the circuit to ensure the current cannot reverse direction. This allows the field to sweep up quickly and then gradually drop back to zero. Magnet heating limits pulses to every 30-45 minutes.
A key limiting factor in pulsed field experiments is the volume available for the sample. Superconducting or dc magnets often have a bore of 30 – 50mm. Cryogenic dewars used during the experimental usually decrease the experimental volume to ~ 15mm of sample space, even if restricted by the smaller diameter of a $^3$He refrigerator. The bore of the pulsed magnets are smaller (14 mm). This limits the sample space to ~ 4mm, after accommodating the cryogenic vessels in the magnet.

Measurements in a short pulse magnet (rise time ~ 8 ms) can be difficult due to the vibrations created during the field sweep due to the quick release of energy. For comparison, typical magnetic field sweep rates for superconducting, resistive and pulsed magnets are 0.35, 4, and 7500 T/min., respectively. The rapid change in field produces experimental pitfalls such as heating in conducting samples and transient effects in the measured signal. [69] Signal noise acquired in the data makes measurements of high frequency quantum oscillations or subtle changes in magnetoresistance nearly impossible. High currents are used to increase the signal to noise ratio. High frequency ac methods can be used (several kHz) to measure sample resistance. However, but for the measurements in pulsed fields described in the following chapters we used a true, non-alternating dc current.
CHAPTER 4
THE TAU-PHASE SYSTEMS

4.1 Crystal structure and properties without a magnetic field

The quasi-two-dimensional (Q2D) organic conductor \( \tau-(P-(S,S)-DMEDT-TTF)_2(AuBr_2)_{1+y} \) has an atypical structure which is unique to charge transfer salts. Both pyrazino and EDO molecules have a variety of different configurations. In the stoichiometry, \( \tau-(P-(S,S)-DMEDT-TTF)_2(AuBr_2)_{1+y} \), \( P \) stands for the pyrazino (nitrogen) species of the donor. The methyl groups protruding from the “legs” at the end of this asymmetric molecule, can extend with one group up and the other down from the plane of the donor, resulting in a \((S,S)\) isomer. If the groups reverse positions, it results in a \((R,R)\) molecule. If these two isomers are randomly distributed through the material, it is referred to as racemic, noted by \((r)\).

![Figure 4.1.1. End-on view of a single conducting layer in the ab-plane. Shaded and unshaded rectangles represent donors of opposing orientations. Circles represent the end view of linear anions.](image)

The length of the donor molecules lies along the c-axis where the donors create a square grid (Fig 4.1.1). Of the “1+y” electron acceptors, the “1” contribution lie within the donor grid, aligned with the c-axis (the circles of Fig. 4.1.1). The “y” portion lie in the \(ab\)-plane between the conducting tiers of the donors and anions, creating insulating layers. Rather than a normal 2:1 (cation:anion) ratio, this class of materials has a ratio of 2:(1+y). The orientation of the anions changes back and forth 90° with each layer. The value of “y” was first assumed to be \(\sim 0.75\) [70]. The imprecise number of anions per unit cell is one of the factors which make the tau systems
very complex. Studies over the last decade have demonstrated the possibilities of varying concentration of the anion sites from time dependence [71] and incomplete chemical reactions in the electrocrystalization process as well as superstructure in the donor lattice [11]. The Fermi surface is heavily dependent of the value of this anion factor which is discussed in our conclusions (Section 4.4). Due to the lack of symmetry, four of the grid layers are needed for a repeating pattern, resulting in a very long $c$-axis ($a \times b \times c \sim 7.4 \times 7.4 \times 68.0$ Å$^3$) in the tetragonal unit cell.

Figure 4.1.2. (a) Fermi surface of the tau-phase materials. (b) Band structure from tight-binding calculations. Solid lines for Fermi surface and Fermi level are for the $y \sim 0.75$ estimate where the dashed lines represent $y = 0$. (taken from Ref. 72).

Several important factors regarding the band structure and Fermi have been observed and studied (see Figure 4.1.2). Arita et al. [6] found that the electrons repulsively interacting through Coulomb forces near the very flat band have a tendency towards ferromagnetism. As a magnetic field is applied the electrons become polarized and are then shifted towards the portion of the
band with a larger dispersion. This lowers the effective mass of the electrons, resulting in increased conductivity. Experimental observations of negative magnetoresistance at low fields agree with this hypothesis. The band structure is also critical to explaining results from higher field studies. With the Fermi level so close to the energy gap (a) the lattice could be distorted to cause the upper band to rise and Fermi level to fall into the gap or (b) the Fermi level could shift due to magnetism. We discuss this possibility further in section 4.4. The band structure may be partially correct but the proposed Fermi surface (~ 950 tesla) does not match the experiment values for pyrazino or EDO measurements [9,73].

Table 4.1.1. Transfer integrals determined from extended Huckel tight-binding (EHT) and valence band Hartee Fock (VBHF) calculations. The transfer integrals, t₁, t₂, and t₃ are shown in Fig. 4.1.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal No.</th>
<th>t₁(meV)</th>
<th>t₂(meV)</th>
<th>t₃(meV)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDO</td>
<td>1</td>
<td>206</td>
<td>24</td>
<td>2</td>
<td>EHT</td>
</tr>
<tr>
<td>EDO</td>
<td>2</td>
<td>184</td>
<td>16</td>
<td>---</td>
<td>EHT</td>
</tr>
<tr>
<td>Pyrazino</td>
<td>3</td>
<td>138</td>
<td>16</td>
<td>---</td>
<td>EHT</td>
</tr>
<tr>
<td>EDO</td>
<td>1</td>
<td>96.2</td>
<td>0.1</td>
<td>4.6</td>
<td>VBHF</td>
</tr>
<tr>
<td>Pyrazino</td>
<td>3</td>
<td>78.2</td>
<td>0.2</td>
<td>6</td>
<td>VBHF</td>
</tr>
</tbody>
</table>

Table 4.1.1 shows the results of two variations of the tight-binding calculations where the transfer integrals t₁, t₂, and t₃ refer to figure 4.1 [7,74]. The largest orbital overlap is created by the donors with c-axis orientations which are opposite with respect to each other. The longest sides of these molecules meet at right angles (t₁ in Fig. 4.1.1.). The donors are slightly offset along the c-axis and the atomic sites labeled N, S₁ and S₂ in Fig. 4.1.3 provide the largest interactions. [72,74] As mentioned, note that in the crystal structure these molecules meet at right angles and have been drawn “flat” for the sake of clarity. The strength of the t₁ interaction is roughly ten times that of the t₃ interaction between parallel donors for both the pyrazino and EDO type of donors.
The temperature dependence of a racemic pyrazino sample is shown in Figure 4.1.4. The nitrogen-based tau materials, regardless of isomer, have a resistance which rises with decreasing temperature. Near 12 K a low resistance point is observed before a quick increase. The metallic character of materials is often estimated from the residual resistivity ratio (RRR). For this sample, \[ \frac{R(300K) – R(4.2K)}{R(4.2K)} \sim -1, \] in comparison with typical metals which often have a value closer to 100.
4.2 Results of Transport and Thermodynamic Experiments at Ambient Pressure

Figure 4.2.1. Magnetoresistance for τ-AuBr$_2$ measured in dc fields to 33 tesla at T = 0.5 K. The field is aligned with the c-axis of the crystal. The arrows indicate the field upsweep versus downsweep.

In all tau systems, negative magnetoresistance is observed in low fields. A magnetic transition has not yet been proven but a large hysteresis is observed between the upsweep and downsweep resistance curves, suggesting a change in the ground state (Figure 4.2.1). Further, preliminary electron spin resonance measurements show an increase in adsorption near the proposed phase boundary below 20 K, indicating magnetic ordering. Following this initial drop in magnetoresistance, the system remains in a metallic state in the region ~ 10–35 tesla.

Shubnikov de Haas (SdH) oscillations were first studied for the tau materials in magnetic fields to 33T. A simple calculation of the ratio of the star-shaped Fermi surface area expected from theory and the entire first Brillouin zone would produce a SdH frequency of nearly 950 T. Fast Fourier transform analysis of magnetoresistance data revealed several quantum oscillation frequencies, all of them lower than the predicted one. Following the notation of Ref. A9, low and high SdH frequencies of F$_l$ ~ 185 T and F$_h$ ~ 515 T were found, with effective masses of $m_e^* ~ 4.4 m_e$ and 7.5 $m_e$, respectively. The higher frequency is more easily resolved from the FFT spectrum. In the case of τ-EDO-AuBr$_2$, masses of 1.6$m_e$ and 3.5$m_e$ are found from frequencies of 50 T and 481 T, where the lower frequency is dominant of the FFT. In short, though isostructural, the effective mass of the majority carriers in pyrazino for frequency, F$_h$
have an effective mass that is almost five times larger than in EDO, suggesting the electron dynamics of pyrazino are on the border between Fermi gas and liquid.

Magnetoresistance measurements in pulsed fields to 55 T first revealed the metal-insulator transition demonstrated in Fig. 4.2.2. [76] These measurements of a $\tau$-(P-(S,S)-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, clearly show the resistance rise quickly as the magnetic field increases. It should be noted that the semi-periodic noise of the 4.2 and 6.3K data are not quantum oscillations. This type of noise is regularly observed in pulsed fields due to mechanical vibrations. Also, though the lower temperature resistance data seems to decrease to nearly its
metallic value in the high field limit, it was later confirmed that current through the sample decreases in the insulating state, resulting in a decrease of measured voltage. This transition was observed in temperatures as high as 13K. The threshold field of the transition decreases with lower temperatures. The temperature-field phase boundary is defined as the intersection point between the metallic background signal and the rising magnetoresistance. The behavior of the boundary follows $dT/dB > 0$. This suggests a transition to an insulating state similar to the density wave state of the Bechgaard salts.

Figure 4.2.3. Angular dependence of the metal-insulator transition for $\tau(r)$-AuBr$_2$. The dotted line was used to define the points shown in the inset.

Further measurements [77] clarified that the transition did not meet the criteria of a field-induced density wave. The angular dependence of the transition confirmed it was, in fact, a bulk transition. Therefore, it did not follow the $1/\cos(\theta)$ dependence of an orbital effect, such as a spin density wave (Fig. 4.2.3). (In all measurements of angular dependence for the tau materials, $\theta$ represents the angle between the applied magnetic field and the $c$-axis of the crystal). Further, the magnetoresistance of the $\tau(r)$-AuBr$_2$ sample did not show a gradual change in magnetoresistance or any cascade-type effects. Instead, near $\sim 35$ T, the system went from a Q2D metal to a complete insulator. The metal-insulator transition shows a weak angular dependence with a shift
of less than 1 tesla as the sample is rotated from B // \(ab\)-plane to B // \(c\)-axis at the base temperature (0.5 K).

In all of the experimental techniques used to better understand the nature of the phase transition, effects in the material \(\tau-(\text{P-}(r)-\text{DMEDT-TTF})_2\text{(AuBr}_2\text{)}_{1+y}\) seemed the most acute. The transition was not limited to samples containing this specific donor molecule but the transition occurred consistently at slightly lower threshold fields. The disorder associated with the varying bond angle of the methyl end groups could play a role in the transition from metal to insulator, but this has not been confirmed. This variety of sample was selected for skin depth, magnetocaloric, and magnetization experiments which are described in subsequent paragraphs.

![Figure 4.2.4. Tunnel diode oscillator measurement of skin depth for \(\tau-(\text{P-}(r)-\text{DMEDT-TTF})_2\text{(AuBr}_2\text{)}_{1+y}\). The solid arrows indicate the direction of the field sweep while the dotted arrows show the phase boundaries.](image)

In pulsed fields, a measurement of skin depth was completed using a tunnel diode oscillator circuit. Samples of \(\tau-(\text{P-}(r)-\text{DMEDT-TTF})_2\text{(AuBr}_2\text{)}_{1+y}\) were stacked into a small coil which produces a rf field of \(\sim 43\) MHz. The magnetic field was swept at different temperatures as high as 18K. The highest temperature data was used as a background signal and subtracted from the other measurements. During the magnetic field upsweep, the frequency of the circuit
dropped at the phase boundary (Fig. 4.2.4). The frequency shifts again during the downsweep at a different value of field, agreeing with the hysteresis observed in all measurements.

The behavior of the skin depth, $\delta$, with changing conductivity ($\sigma$) can be seen from the formula,

$$\delta^{-1} = \frac{1}{2} \sqrt{\frac{\varepsilon \mu}{\omega}} \left( \sqrt{1 + \left( \frac{\sigma}{\varepsilon \omega} \right)^2} - 1 \right)^{\frac{1}{2}},$$

where $\omega$ is the circuit frequency, and $\varepsilon$ and $\mu$ are the permittivity and permeability, respectively. The skin depth increases during the upsweep of the magnetic field as the conductivity decreases to zero. Following the threshold field, the sample is transparent to the rf field from the circuit as the skin depth becomes larger than the sample dimensions. The maximum of the derivative of the data was used to determine the phase boundary (dotted arrows in Fig. 4.2.4).

![Figure 4.2.5. Magnetocaloric effect observed from $\tau-(P-(r)-DMEDT-TTF)_{2}(AuBr_{2})_{1+y}$ in dc magnetic fields.](image)

A magnetocaloric measurement was also undertaken to examine the thermodynamic nature of the phase transition. A Ruthenium oxide thermometer was sanded down to a small fraction of the initial thickness in an effort to create a low mass sample platform sensitive to exothermic or endothermic transitions. A $\tau-(P-(r)-DMEDT-TTF)_{2}(AuBr_{2})_{1+y}$ sample was attached to the thermometer using Apiezon N grease to ensure a good thermal link. The thermometer resistance was monitored using a standard four terminal configuration. The
measurement was first carried out in pulsed magnetic fields where the thermometer and sample were in contact with $^3$He exchange gas. A shift in temperature was observed in both the upsweep and downsweep following the same hysteretic behavior which was previously observed in magnetoresistance. The experiment was repeated in an evacuated sample chamber in dc fields where the sweep rate for the magnet is at least five orders of magnitude slower. A clear exothermic reaction was observed after subtracting the background signal. The amplitude of the signal grew with decreasing temperature as one would expect for a better established ground state as the temperature approached zero.

Figure 4.2.6. Shubnikov de Haas oscillations observed for $\tau$-(P-(S,S)-DMEDT-TTF)$_2$(AuI$_2$)$_{1+y}$ near the metal-insulator transition. Inset (top): Upsweep of the same data analyzed for peak-to-peak closed orbit frequencies. Inset (bottom): Sample current through $\tau(r)$-AuBr$_2$ during the high field phase transition.

The magnetoresistance of other variants of the tau systems besides the racemic donor were measured with similar results. The magnetoresistance of $\tau$-(P-(S,S)-DMEDT-TTF)$_2$(AuI$_2$)$_{1+y}$ was measured along the c-axis of the sample in dc fields to 45 tesla. As expected, the MR increased near 41 T during the upsweep and returned to a metallic state at $\sim$ 36 T during the downsweep (Fig. 4.2.6). Quantum oscillations were easily observed in both increasing and
decreasing fields thereby demonstrating the existence of a 2D Fermi surface next to the edge of the phase boundary. As shown in the top inset to Fig. 4.2.6, the high field oscillations preceding the transition (measured peak to peak) have larger frequency values than previously observed, though the amplitude of the oscillations grow with increasing field, as expected from Lifshitz-Kosevich formalism.

Many of the magnetoresistance measurements are saturated at high fields. Experiments to monitor the sample current were used to determine if the maximum resistance which was measured reflected the true value of the resistance. To measure this, a shunt resistor was placed in series with the sample and its voltage was monitored while the magnetic field was swept. When the magnetoresistance of the sample begins its abrupt increase, the current begins to fall to zero (Fig. 4.2.6., lower inset). No current flows through the sample in the insulating state. As the magnetic field is lowered past the transition field, current once again flows through the sample. If the current estimated from this procedure in the high field limit for $\tau(r)$-AuBr$_2$ is used to calculate the resistance from Ohm’s law, the resistance rises from 10 $\Omega$ (near 20 T, in the metallic region) to $\sim$ 50 M$\Omega$ (near 45 T).

Following these measurements several properties of the phase transition have been clearly established: (1) the transition is strongly hysteretic, indicating it is first order, (2) it is a bulk transition and no dependence on orbital effects and (3) the clearly defined Fermi surface completely disappears beyond the phase boundaries in higher fields. The parameters of the transition were established with the preceding experiments but the mechanism for the MI transition required further experiments. For this reason, measurements were undertaken exploring the magnetization, thermopower, and pressure dependence as well as the magnetoresistance of single crystals with the EDO donor for comparison.

Magnetization measurements using a capacitance cantilever are not very sensitive to small changes in magnetic moment. As a result, a PRC120 cantilever was used for this measurement. $\tau(r)$-AuBr$_2$ and $\tau$-EDO- AuBr$_2$ samples with dimensions of approximately 1 x 1 x 0.5 mm$^3$ and masses of 0.5 mg were attached to cantilevers using 5 minute epoxy. The arms (sample and reference) of the cantilever were added as two branches of a bridge resistance circuit, as described in chapter 3. Fig. 4.2.7 shows the results for EDO and pyrazino for comparison. De Haas van Alphen oscillations are observed for the EDO sample in the B // c-axis ($\theta = 0^\circ$) orientation. Oscillations were not observed for the pyrazino sample, although a clear increase
(decrease) in the magnetization was observed during the upsweep (downsweep) at the metal-insulator phase boundary. No such transition point was obvious in the EDO data, even in the $\theta = 90^\circ$ orientation, where there were no oscillations in the signal. As described in chapter 3, due to the high sensitivity of the cantilever, it is difficult to resolve the contribution to the torque from the mass of the sample rather than the magnetization. The data is most easily analyzed by subtracting a term fit to the background.

Following the subtraction of the background a magnetization envelope which looks similar a hysteresis curve of a ferromagnet, is observed in fields swept up to the maximum and down below the phase boundary (Fig. 4.2.8). The angular dependence (inset to Fig. 4.2.8) shows change in overall signal from $\theta = -17.5^\circ$ to $90^\circ$. The quantitative value of the magnetization was estimated from a previous cantilever calibration measuring the Meissner effect of a high purity lead sample. When the field was swept to the maximum limit and then decreased below the metal-insulator phase boundary a hysteretic envelope was observed (outlined by the black arrows of figure 4.2.8). In cases where the field was stopped and then reversed during the upsweep (the
points shown by the blue and orange dotted arrows), but not yet to the field maximum, the signal crossed the envelope and followed the downsweep magnetization path to lower fields (solid blue and orange arrows). The same behavior was observed by stopping and then increasing the field during downsweeps (dotted and solid green arrows). Interestingly, reversibility of the magnetization was observed as the field is swept down (dotted red arrow) to 36 tesla, then swept up to 40 tesla and then back down to lower fields (solid red arrow). In the range 36 – 40 tesla, the magnetization data was fully reversible along the same path (double-ended red arrow). We also studied the angular dependence of the magnetization. Maxima from the derivatives were used to define the metal to insulator transition. The phase boundary produced was identical to what was found from magnetoresistance measurements.

Figure 4.2.8. Magnetization envelope for $\tau(\tau)$-AuBr$_2$ showing reversible, hysteretic paths ($T = 0.5$ K). Inset: Angular dependence of the raw (background included) cantilever measurement. See text for details.

Magnetization was also measured in pulsed magnetic fields using a susceptibility coil (Fig. 4.2.9). The signal of the coil was measured at low temperature both with and without a
sample inside the coil, so a background signal could be determined. A deviation from a linear increase in signal is observed with the sample in place. The threshold field for this increase closely follows the metal-insulator phase boundary. Previous calibrations of the coil provided a quantitative estimate of the magnetization. The amplitude of pulsed and dc field magnetization measurements are in general agreement.

![Graph](attachment:image.png)

Figure 4.2.9. Magnetization signal from τ(r)-AuBr₂ using a susceptibility coil in pulsed fields.

Using a sample of τ-(P-(S,S)-DMEDT-TTF)₂(AuI₂)₁+y, magnetothermopower measurements were carried out in an evacuated sample chamber in dc fields of 42, 43.5, 44.2 and 45.1 tesla (Fig. 4.2.10). The steep slope of the thermopower in the metallic regime suggests a large density of states (small bandwidth) near the Fermi level, which is consistent with band structure calculations. The behavior of the thermopower indicates an energy gap which can be extracted using the slope of the signal using $S(T) \sim \frac{E_{\text{gap}}}{T}$. Using the field values available it is clear that a gap begins to open near 42 tesla and widens as the field increases (Fig. 4.2.10, inset).
Fig. 4.2.10 shows the angular dependence of $\tau$-EDO-AuBr$_2$ on angle. The large oscillations, previously observed by Konoike et al.,[73] reach the $n = 1$ Landau level at the high field limit. The sample was rotated from 0° (where B $\perp$ ab-plane) to 30°, 60° and 90° (B $\parallel$ ab-plane). As expected, the quantum oscillations decay and shift to higher frequencies as the angle is increased, but an upturn in high field magnetoresistance remains. This can be understood from the fact that the EDO systems may also experience the same high field behavior as the pyrazino samples, but to a much smaller extent. While the pyrazino samples become bulk insulators in high fields, the EDO samples just exhibit an increased magnetoresistance. As with the pyrazino experiments the transition occurs at all orientations of the sample to the field. Further evidence of this is observed when the EDO oscillations are plotted versus inverse field, resulting in a non-Dingle rise in amplitude at the highest peak.
4.3 Magnetotransport Under Pressure

For all varieties of tau samples a small valley was observed in the cooldown curve (Fig. 4.3.1). There is a more acute deviation in the cooldown curve of the pyrazino systems, similar to a step, around 12K. In contrast, for the oxygen-based materials a broad minimum is observed near 50 K. The temperature curves at a pressure of $\varepsilon_1$ above are very similar to previous ambient pressure measurements. With the addition of pressure, the minimum for EDO shifts slightly towards lower temperatures. However, the opposite is true for the pyrazino materials where the resistance step shifts to higher temperatures with an increase in pressure.
In an attempt to suppress the onset of the insulating state, three samples were mounted in a the B $\perp ab$-plane orientation in a pressure cell: $\tau$-AuBr$_2$, $\tau(r)$-AuBr$_2$, and $\tau$-EDO-AuBr$_2$. The pressure of the cell was increased to 2.5 kbar, which decreased to ~ 1 kbar during the cooldown to liquid helium temperatures. Fig. 4.3.2 shows the resulting magnetic field dependence for all three samples. Clearly, only 1 kbar of pressure produces a 2D plane with large molecular orbital overlap as demonstrated from the increasing amplitude of the quantum oscillations in the allowed range of field. More of a surprise is the influence of a cell with only “fingertight” pressure (the top clamp of the pressure cell is only tightened by hand). A positive pressure, $\varepsilon_1$, results at low temperatures from the solidification of the pressure medium. Even only manipulated by this minor pressure, the overlap is still improved for the nitrogen-based systems and quantum oscillations persist into the onset of the insulating state. The EDO results also show an increase in MO overlap by the clear oscillations peaks at ~ 34, 37, and 40 tesla, corresponding
to the 500 T orbit frequency. These peaks are barely resolvable in previous results at ambient pressure. [73]

Figure 4.3.2. Pressure dependence of the magnetoresistance of (a) τ(τ)-AuBr₂ (b) τ-AuBr₂ and (c) τ-EDO. For each panel the left (right) axis corresponds to a pressure of ε₁ (1 kbar).
Figure 4.3.3 shows the temperature dependence of the SdH oscillations. The nitrogen-based systems (Fig. 4.3.3a and 4.3.3b) show a large increase in the SdH oscillations amplitude at low temperatures. Without pressure, quantum oscillations were not previously observed in a racemic sample. A small positive background magnetoresistance is observed in the high field limit it is not large enough to suggest the systems are approaching the metal to insulator
transition. FFT analysis of the EDO results using only the field range 11.5 to 27 tesla do not show a peak for the ~500 T orbit frequency. Using the entire range of field (11.5 to 45.1 tesla), a higher frequency peak is seen in the FFT spectrum. The higher frequency oscillations are clearly superimposed on the background magnetoresistance created by the fundamental EDO frequency ~50 T (Fig. 4.3.3c).

![Graph](image)

Figure 4.3.4. Fast Fourier Transform spectra of (a) \(\tau(r)\)-AuBr\(_2\) (b) \(\tau\)-AuBr\(_2\) and (c) \(\tau\)-EDO under 1 kbar of pressure for temperatures 4.3, 3.5, 3.15, 2.8, 2.2, 1.8, 1.4, 1.2, 1.0, 0.75, and 0.5 K.

The fast Fourier transforms (FFT) of the same samples are shown in Fig. 4.3.4. The pyrazino sample has a dominant frequency of 508 T, which is slightly larger than the frequency observed for another sample at ambient pressure [9]. An increase in frequency can be expected as pressure decreases the lattice parameters of the system and real-space area for the electron
orbits increases. A smaller peak at 186 T is consistent with pressure results without pressure. The racemic sample shows a lower frequency of 495 T and a secondary peak of 185 T. The frequencies are most easily observed below 2.2 Kelvin, whereas at ambient temperatures the oscillations were only seen below 1.2 Kelvin. The 58 tesla slow oscillations of the EDO system dominate the spectrum shown in Fig. 4.3.4c. A second harmonic peak is seen at 120 T, along with a peak near 200 T and one at 483 T. These results nearly match the observations of Konoike et al. [73] with frequencies of 50 T and 481 T. A different sample of the pyrazino variety was measured in a portable dilution fridge at 5 kbar and 205 mK. A frequency of 542 T was observed. The estimated shift of the nitrogen-based systems with frequency is ~ 1.5%/kbar. Estimating from the $\varepsilon_1$ and 1 kbar frequencies measured, the shift for the frequencies of EDO is much larger, ~ 21%/kbar.

The effective masses were measured using the amplitudes of the FFT peaks from the dominant frequency of each material. The value is found by from Equation 2.1.9 which provides a fit for $R_T$. This is the oscillation damping factor introduced from frequencies differing due to the finite temperature [78]. As expected, the effective mass decreased in the case of the nitrogen-based systems from approximately 7.5$m_e$ to 5.8$m_e$. Basically, pressure improves the molecular orbital overlap and the material becomes more metallic. The effective mass of the EDO sample dropped from 1.6$m_e$ [73] to 1.09$m_e$. The masses extracted from these fits were used to fit the Dingle damping factor, $R_D$ (Eq. 2.1.10), which gives a measurement of the scattering of the conduction electrons. The amplitude of the resistance peaks is plotted versus inverse magnetic field. As noted in chapter 2,

$$T_D = \frac{\hbar}{2\pi k_B \tau},$$

so the Dingle temperature is inversely proportional to the scattering rate. The Dingle temperature in ambient measurements is similar for the pyrazino and EDO materials, ~ 1.4 K. The Dingle temperature of $\tau$-AuBr$_2$ (Fig. 4.3.5e) decreases because the scattering time improves under pressure. A Dingle temperature of 1.80 K was measured for EDO, contrary to the expected result. In this case the slow oscillations produced only four peaks over the entire range of field, making the fit very inaccurate. Table 4.3.1 provides a summary of the frequencies observed and effective masses calculated.
Figure 4.3.5. Effective mass plots for (a) τ(r)-AuBr₂ (b) τ-AuBr₂ and (c) τ-EDO. Dingle plots fitting the amplitude of oscillation peaks for (d) τ(r)-AuBr₂ (e) τ-AuBr₂ and (f) τ-EDO. Effective mass and Dingle temperature values are noted in each panel.

Table 4.3.1. The SdH frequencies observed for τ(r)-AuBr₂, τ-AuBr₂, and τ-EDO-AuBr₂ at the pressures indicated. F₁, F₂, and F₃ signify the low, intermediate and high frequencies observed. Values in parenthesis indicate the effective masses found from those frequencies.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Frequency</th>
<th>τ-(r)AuBr₂</th>
<th>τ-AuBr₂</th>
<th>τ-EDO-AuBr₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε₁</td>
<td>F₁</td>
<td>-----</td>
<td>-----</td>
<td>47.3</td>
</tr>
<tr>
<td>1 kbar</td>
<td>F₁</td>
<td>-----</td>
<td>-----</td>
<td>58 (1.09)</td>
</tr>
<tr>
<td>ε₁</td>
<td>F₂</td>
<td>166</td>
<td>175</td>
<td></td>
</tr>
<tr>
<td>1 kbar</td>
<td>F₂</td>
<td>185 (3.55)</td>
<td>185 (3.33)</td>
<td>200 (1.19)</td>
</tr>
<tr>
<td>ε₁</td>
<td>F₃</td>
<td>497</td>
<td>505</td>
<td>465</td>
</tr>
<tr>
<td>1 kbar</td>
<td>F₃</td>
<td>494 (5.73)</td>
<td>507 (5.84)</td>
<td>484 (2.18)</td>
</tr>
<tr>
<td>5 kbar</td>
<td>F₃</td>
<td>-----</td>
<td>537</td>
<td>-----</td>
</tr>
</tbody>
</table>
The velocity of the electron ($\hbar k_F = m^* v$) can be estimated using the area of the Fermi surface in k-space to find the Fermi wavevector ($A_k = \pi k_F^2$). Using the relaxation time from the Dingle temperature we can find the mean free path of the electrons can be determined from $l = \nu \tau$. The pyrazino materials have a path of $\sim 100$ Å, while the value is nearly three times greater for the oxygen-based materials.

### 4.4 Discussion: The Metal-to-Insulator Transition

The metal to insulator transition in the tau systems is fascinating for both its lack of subtlety and the very high region of magnetic field in which it occurs. The results are repeatable for a number of different derivatives of the tau-phase materials. The many experiments conducted thus far have allowed us to continue to explore some possible origins to the transition while eliminating others. Below, we review some of the key points of the findings as well as propose several experiments that could potentially clarify remaining questions.

The pressure dependence of the materials provides the strongest evidence that the lattice is “loosely” bonded. The two-dimensional conducting planes are created via the $\pi$-orbital overlap over the donors at right angles. The pyrazino materials show clean SdH oscillations to 45 tesla, under only 1 kbar of pressure. The EDO materials, which have a limited but observable high field transition, also show increased metallic character under pressure. In addition the high field background magnetoresistance in the EDO compound is removed.

This type of behavior has been previously observed for a 2D material. K-(ET)$_2$Cu[N(CN)$_2$]Cl has a complex unit cell with “polymeric” anions (i.e. the chain-like Cu[N(CN)$_2$]Cl anions make up the insulating layer). [79] The system is described as having loosely bound donors which are susceptible to perturbations. While this model does not provide an explanation for the phase transition it illustrates an example of this behavior. In both cases, transitions may be brought about by the sheer complexity of the systems and an inability to maintain long range order under extreme conditions, such as very high fields.

Recent structural measurements of the tau-type materials may, at least, provide an explanation of the differences in the measured Fermi surface. Konoike et al., [11] measured the x-ray diffraction (XRD) pattern of oxygen-based (EDO) crystals. A superstructure was found
which changes the unit cell of the conducting layers to \(2a \times 2b\). Using these new parameters, the band filling “\(y\)” is found to be \(\sim 0.875\) and the Fermi surface is reconstructed as shown in Fig. 4.4.1. [80] The smaller pockets may account for the lower observed frequency of the EDO materials. XRD measurement of the pyrazino materials have not shown any superstructure, even down to 14 K.

Yoshino et al. conducted an interesting experiment to test the effect of changing the “\(y\)” factor of the anions in EDO materials. [81] With successively higher temperature heat treatments Yoshino found that the “\(y\)” anions would decrease but the lattice parameters would not change. The overall effect was a lower band-filling. This was observed in the temperature dependence as untreated samples showed metallic character and treated samples became semiconductors. High field measurements of treated versus untreated samples showed a decrease in SdH frequency for both treated EDO and pyrazino samples. The significance of the “\(y\)” anions was apparent from the results, however this value is still not known with certainty. The band structure of EDO was recalculated in Ref. 81 and the results do not show a flat band. The Fermi level of EDO for \(y = 0.875\) is well above the band edge and rises further for lower values of “\(y\)”.

Figure 4.4.1. New Fermi surface of the EDO material, taking into account the superstructure (from Ref. 9).
The cooling data at $\varepsilon_1$ and $\sim 1$ kbar of pressure shows differences between the EDO and pyrazino types of molecules. The racemic and pyrazino samples show almost identical behavior where the resistance minimum near 12K at low pressures shifts $\sim 4$K/kbar to higher temperatures. At almost the same rate, the minimum of the EDO sample cooldown curve shifts to lower temperature, suggesting that the minima do not have the same origin. A shift to higher temperatures is more typical of ordering, in which coupling is enhanced by pressure. A shift to lower temperatures most likely indicates a better molecular orbital overlap. Overall, the resistance of the EDO sample drops 50% while cooling but returns to nearly the 300 K value at base temperature. The nitrogen-based sample rises at least one order of magnitude in resistance over the temperature regime.

Table 1 shows that for two types of calculations, the transfer integrals for EDO are stronger than for pyrazino materials. As a result, the metal-insulator transition is much more dramatic for the pyrazino systems. It could be attributed to weaker molecular orbital overlap for the pyrazino materials. Oxygen belongs to the group of elements known as chalcogens. Sulfur and selenium also belong to the same group and are often substituted in among the carbon atoms of donor molecules. For example, the common donors TMTSF, BEDT-TTF, and TTF all contain either S or Se. As mentioned in section 4.1, the sulfur atoms of the DMEDT-TTF donors which interact with the nitrogen (or oxygen) atoms of the adjoining donors. The similar orbital properties of the oxygen and sulfur sites result in a better overlap and therefore afford more metallic character.

Proton nuclear magnetic resonance showed a distinction between magnetic ordering for the EDO and pyrazino materials. Below 20 K, a pyrazino single crystal showed a broad peak in the relaxation rate whereas the EDO system did not. Magnetism is the most interesting possibility of the cause of the metal-insulator transition. If the applied field were coupled to the lattice, a slight distortion could reconfigure the band structure above the Fermi level. This would be consistent with the thermopower results which demonstrate that pyrazino materials have a rapidly increasing energy gap in high fields. The magnetization results strongly support a magnetic mechanism with the reversibility and large hysteresis. Though the magnetic signal is weak, it was only observed in the pyrazino system in the cantilever measurements. Without magnetic elements in the crystal structure or spin moments, the origin of the magnetism remains a question. Hysteresis is observed in all experiments which provides evidence the phase
transition is first order. Further, the magnetocaloric measurements confirm that the transition involves a latent heat.

The abruptness and magnitude of the transition, as well as the sample current suggests that conduction paths are removed from the system entirely. A perturbation which could distort the lattice would be difficult to detect at fields as high as 40 tesla. Though pressure may shift the transition to higher fields or completely suppress it, a measurement with strain on the sample may induce it at lower fields. While the experiments mentioned above suggest a first order transition, a specific heat measurement would be more conclusive. X-ray diffraction or neutron scattering would provide irrefutable evidence of a change in the lattice however experiment facilities are not yet available for these measurements. Among the impediments to these experiments are the low temperatures and high fields required as well as the small samples which are available.
CHAPTER 5
DENSITY WAVE STATES IN (PER)$_2$M(MNT)$_2$ (WHERE M = AU, PT)

5.1 Crystal Structure and Temperature Dependence

The perylene-based organic materials, (Per)$_2$M(mnt)$_2$, have been studied for three decades because of their interesting and widely varying properties. These materials provide a good approximation of a one-dimensional metal due to high anisotropy and conductivity along one axis. The conducting chains are created by the stacking of the perylene donor molecules. Anion chains contain M(mnt)$_2$ molecules, where mnt = maleonitriledithiolene and M is a metal atom (either Au or Pt, for the results reported here). There is almost no interchain coupling between the molecular stacks of donors and anions. In cases where the metallic site of the anion has spin (e.g. M = Pt, S = ½) measurements have shown magnetic characteristics. [25] The crystal structure of the M = Au and M = Pt systems is identical but the Au sites on the anion chains are spin zero. This allows for comparison of the behavior of the two materials to observe the effects of spin chains. The application of strong magnetic fields results in a phase transition from a low temperature, insulating CDW state to a metal. In higher magnetic fields, (Per)$_2$Pt(mnt)$_2$ forms a new density wave state, which has been studied systematically for temperature, angular and pressure dependence.

The crystal structure is monoclinic ($a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$) with unit cell parameters for $a$ and $b$ of 16.61 and 4.19 Å, respectively, and $c \sim 25.5$ (26.6) Å ($ac$-plane shown in Fig. 5.1.1). [40] The donor molecules form a tilted stack with a separation of $\sim 3.30$ Å, where the normal of the molecular plane is $37^\circ$ from the $b$-axis. [23] The M(mnt)$_2$ molecules are spaced 3.65 Å apart and tilted in the same manner as the donors but $29^\circ$ from the $b$-axis. [82] X-ray diffraction experiments were performed on an unusually large single crystal to determine the crystallographic axes. The $b$-axis is along the longest dimension of the needle-like crystal while the width and height follow the $a$ and $c$ axes, respectively. The single crystals measured were typically on the order of 100 x 2000 x 20 $\mu$m$^3$ ($a \times b \times c$ axes).

Thermopower measurements confirm that the materials are metallic at higher temperatures with hole carriers. Full charge transfer is assumed from the partially oxidized
(Per)$^{1/2}$ molecules leading to 3/4-filled bands. [83] Bandwidths of $W \sim 0.60$ eV were obtained in the direction of the $b$-axis. [40] An extended Huckel Hamiltonian was used to calculate the transfer integrals in each direction of the unit cell. [84] The intrachain bandwidth, $t_b \sim 0.147$ eV, agrees with the thermopower measurements and the calculations yield an overall ratio of $\sim 150 : 2.0 : 0.1$ meV for $t_b : t_a : t_c$, resulting in a highly one-dimensional system.

The perylene materials go through a Peierls distortion at low temperatures. X-ray scattering experiments revealed typical precursor lattice distortion through satellite sites for a number of the perylene materials with higher transition temperatures (M = Cu, Ni, Co, and Fe with $T_c = 33, 25, 73$ and $58$, respectively). [85] With a $T_c$ of only 8 K for M = Pt, precursor effects were observed below 25 K but the transition temperature could not be reached with the x-ray measurement equipment. [24] Though M = Au has a higher transition temperature of 12 K, no structural changes were observed from x-ray measurements. For these two materials, the CDW ground state has been confirmed by resistivity and nonlinear IV characteristics common to CDW systems as well as comparison with the behavior of higher temperature systems [86,87].

Figure 5.1.1. The lattice structure of the $ac$-plane of (Per)$_2$M(mnt)$_2$. The M(mnt)$_2$ molecule is located at the center of the unit cell with the M (metal) site in the center of the molecule. Six chains of donor molecules surround each anion chain.

The susceptibility of the M = Au ($S = 0$) system is almost static (Pauli-like) over the entire temperature regime to the transition temperature were the signal disappears as the electrons localize. The susceptibility of M = Pt ($S = \frac{1}{2}$) follows Curie-Weiss behavior from room
temperature to ~ 30 K. The M(mnt)₂ molecules of the M = Pt compound become dimers at the spin-Peierls transition temperature, resulting in a rapid decrease in measured susceptibility. [88,25,83] This magnetic transition is independent of field orientation, confirming it was a lattice instability rather than driven by the applied field. Both the Peierls transition in the donor stacks and spin-Peierls in the anion stacks take place at the same temperature. This suggests there is a strong possibility of coupling between the chains but this is still being debated. The conclusions of ref. 24 state that the spin-Peierls distortion in the S = ½ chain drives the metal-insulator transition in the conducting chain while ref. 30 suggests the transition are independent.

![Figure 5.1.2. Zero-field temperature dependence of M = Au and M = Pt. Arrows indicate the axis corresponding to the resistance of each sample.](image)

The anisotropy, as measured by the Montgomery method, for the conductivity (σ) of the perylene systems is on the order of \( \frac{\sigma_0}{\sigma_\perp} \sim 10^3 \). [31] Charge transport is nearly confined to the \( b \)-axis. As the energy gap opens as the CDW state forms, a rapid increase in resistance is observed. The transition temperature has shown a sample dependence in our measurements and others [89]. Deviations are usually not larger than 1K and questionable results have been disregarded. Though
the temperature at which a minimum in the resistance is observed occurs at higher temperatures, $T_c$ is defined as the peak of $d(ln(R)/d(1/T))$. This point occurs on the slope of increasing resistance for temperature dependence data (fig. 5.1.2). The slope of the $M = Pt$ system is often much steeper than that of the $M = Au$ material. Henriques suggests [24] that the gradual resistivity change for $M = Au$ corresponds with the difficulty in observing lattice changes in x-ray measurements.

\[
\text{5.2 (Per)$_2Au(mnt)$_2}
\]

The organic system TTF-TCNQ exhibits a metal-insulator phase transition near 53 K, due to a Peierls distortion. The sample resistance was measured for zero field and 5 tesla cooling curves. [32] The authors found that the change in resistance fit fairly well to

\[
\frac{\rho(B) - \rho(B = 0)}{\rho(B = 0)} = \frac{\Delta \rho}{\rho} = -\frac{1}{2} \frac{(\mu_B B)^2}{kT} \quad \text{(Eq. 5.2.1)}
\]

below the transition temperature. The results were difficult to interpret due to the high transition temperature and small strength of the available magnetic field. Between the cooling curves with and without the applied magnetic field the sample resistance only changed $\sim 1.4\%$.

This experiment was repeated with (Per)$_2Au(mnt)$_2 and (Per)$_2Pt(mnt)$_2 [33]. With available temperatures down to 2 K, the metal-insulator transition was observed in the $M = Au$ sample for the first time. Measurements to 8 T showed a shift in transition temperature which is proportional to the square of the applied field, as expected, but these changes were on the order of 5% and 10% for the $M = Au$ and $M = Pt$, respectively. Further measurements of the $M = Au$ system to 18 T shifted the transition temperature $\sim 15\%$, with no noticeable anisotropy between sample orientations parallel and perpendicular to the applied field.[89]

Matos, et al., continued this work with both the $M = Au$ and Pt compounds. [34] The results for the $M = Au$ material were consistent with previous measurements. The Pt samples showed a strong anisotropy. If the condition, $\mu_B B \ll 2\pi k_B T_c$ is met, then the transition should fit to equation 2.2.10, where the prefactor $\gamma$ is $\sim 0.21$. The $M = Pt$ fit to a lower prefactor by about 10% with the field perpendicular to the conducting axis and closer to 30% in the $B // b$ orientation. In the case of TTF-TCNQ with a transition temperature of $\sim 53 K$ and an applied field of 5 T, the inequality above has a second term which is 100 times larger than the first term.
With a smaller transition temperature of only 12 K for M = Au and applied fields up to 18 T, the second term is only six times larger. Applying higher fields to materials with lower transition temperatures, the mean field description of Tiedje et al., [32] breaks down and a more complicated explanation is necessary.

Figure 5.2.1. Cooling curves for M = Au at fields from 0 to 33 tesla where the field is perpendicular to the conducting axis. Inset: Cooling curves are shown at B = 24 T in the orientations indicated.

For our measurements, the magnetoresistance of a (Per)$_2$Au(mnt)$_2$ sample was measured with a current of 10 $\mu$A using a standard four-contact configuration and lock-in amplifier as described in chapter 3. The field was aligned perpendicular to the conducting axis (B $\perp$ b-axis orientation) and held constant for the data shown in figure 5.2.1. The temperature was slowly increased (~ 1K/min.) using a Neocera LTC-21 temperature controller to adjust the heater current. The lowest temperatures, below 4.2 K, were achieved by using a vacuum pump on the He-4 liquid bath of the cryostat. The sample probe was isolated from the bath, inside a double-walled vacuum sleeve, using He-3 exchange gas as a thermal link to the bath.
As the temperature increased the sample resistance steadily decreased to 10 - 15 Kelvin, depending on the value of the applied field. At this point, a positive slope begins. Comparing the zero-field cooling curve (labeled A) with the data taken at $B = 33$ T (curve H), the resistance drops 88% (measured at 2.5 K) but the CDW is not completely suppressed. The inset to Figure 5.2.1 shows the temperature dependence in both $B // b$ and $B \perp b$ orientations with a field of 24 tesla. With the applied field aligned along the conducting axis the effect of charge ordering is more easily suppressed.

![Figure 5.2.1](image)

Figure 5.2.1. Arrhenius plots from the temperature dependence shown in Fig. 5.2.1. The energy gap has been estimated in the portion of the curve noted by the thick, dotted lines.

In a CDW ground state resistance is activated and expected to follow behavior described by

$$R(T) = R_0 e^{-\Delta/\kappa T},$$

where $\Delta$ is the energy gap. Figure 5.2.2 shows the magnetoresistance data of the previous figure versus inverse temperature, in an Arrhenius plot. The energy gap can be found from fitting the curve, assuming the resistance follows the exponential behavior. At 33 tesla, a gap of 13 K (1.1 meV) is found which is nearly constant between the transition temperature and lowest measured
temperature. Lower field results display a constant energy gap at temperatures immediately lower than the transition temperature followed by a gradually decreasing slope. The thick, dotted lines in the figure show the temperature ranges from which the energy gap was found. Several explanations have been proposed for this type of behavior. For example similar results for (TMTSF)$_2$NO$_3$ have led to the conclusion that the Q1D Fermi surface sheets are imperfectly nested. [90] This is an effect related to strong applied fields coupling to the SDW ground state so this reasoning is unlikely to explain the behavior of the perylene materials.

![Temperature dependence of (Per)$_2$Au(mnt)$_2$ in constant magnetic fields.](image)

Figure 5.2.3 – Temperature dependence of (Per)$_2$Au(mnt)$_2$ in constant magnetic fields. (a) and (b) are the same sample in opposite orientations to the applied fields indicated. (c) A second sample measured in four different orientations with a field of 42 tesla.

Further cooling measurements were undertaken in static magnetic fields as high as 45 tesla. Results shown in figure 5.2.3a and 5.2.3b are for the same sample in perpendicular
orientations. Results below 25 T show very little difference in temperature dependence. In the θ = 0° orientation, the conductance rises three orders of magnitude higher than in the B ⊥ b orientation in a field of 42 T. The orientation dependence is further clarified in figure 5.2.3c where a second M = Au sample was measured using a 1 μA current. The sample was rotated to positions of q = 0, 30, 62 and 90° and temperature dependence was measured at the maximum field. As the orientation of the sample approaches B // b, the slope of the conductance is decreased significantly.

As with Fig. 5.2.2, the sample of figs. 5.2.3a and b does not show typical activated behavior over the temperature range below the transition temperature. A possible cause of this behavior may be Joule heating from the 10 μA current applied. This may be too large a value for samples of very small size. A simple heating model was applied assuming that sample temperature did not follow the measured value of the surrounding exchange gas. Corrections to the sample temperature are shown in the top two panels of figure 5.2.3 using thick, dashed lines.

Figure 5.2.4 Voltage-current characteristics of (Per)₂Au(mnt)₂ at 4.5K. Inset: Temperature dependence of the sample used in the VI measurement which shows a well-defined CDW transition.

CDW ground states are pinned to the lattice by impurities in a crystal. A large enough electric field allows the CDW to depin and slide. This is observed by the point at which current
flowing through a CDW material begins to increase at a nonlinear rate in comparison to the applied voltage. The threshold field ($E_{th}$) was previously measured, without a magnetic field applied, at 4.2K and found to be $\sim 450$ mV/cm. [86] The voltage-current data shown in Figure 5.2.4 was taken by applying a 500 $\mu$s pulse to a M = Au sample at intervals of 10 ms to avoid any possibility of sample heating. The applied current was determined by including a calibrated resistor in series with the sample. The voltages for the sample and resistor were recorded on an oscilloscope. The voltage contacts of the sample were approximately 0.05 cm apart and the data deviates from linearity near 25 mV. The threshold field of 500 mV/cm is agrees with previous results within ten percent.

![Figure 5.2.5. Threshold field for CDW depinning vs. magnetic field for (Per)$_2$Au(mnt)$_2$ in the orientation B // b-axis. Inset: Resistance data of Fig. 5.2.3a, with corrected threshold field values marked at the value where the arrows are pointing for 11.5 and 25 tesla.]

The threshold field ($E_{th}$) necessary to depin the CDW was measured at constant fields and at a temperature of 0.5 K. The voltage of the sample and a resistor were monitored by the sample method described for the zero-field measurement. Using a math function on the oscilloscope
defined as the sample voltage divided by the circuit current, the resistance of the sample was observed. The pulse width and spacing are as describe in the zero-field experiment. When the resistance began to drop, it was assumed that the CDW was becoming depinned. The threshold field was calculated from the distance of the contacts and the results are shown in figure 5.2.5. Threshold fields of 1300 and 700 mV/cm were found at fields of 11.5 and 25 tesla, respectively. The temperature dependence data of figure 5.2.3a is shown as the inset of figure 5.2.5. The measured threshold fields at 11.5 and 25 tesla closely match the voltage values for the sample where non-Arrhenius behavior begins (noted in the inset to figure 5.2.5 by the arrows). It is clear that depinning is the dominant effect preventing expected behavior from the increasing energy gap in decreasing temperatures. The data of figure 5.2.3c was measured using a 1 μA current and follows the expected exponential behavior more closely because the threshold field is never exceeded.

Notice that the minimum field for these measurements is 11.5 T which corresponds to the minimum field of the NHMFL hybrid magnet when the superconducting outsert is maintained at full field. The angular dependence of the magnetoresistance was observed for four separate samples (Fig. 5.2.6). The normalized magnetoresistances of three of them, rotated from B // b (0°) to B ⊥ b (90°), are shown in figure 5.2.6a – 5.2.6c. The sample of figure 5.2.6c shows additional features from using a smaller applied current but the general behavior is the same. The fourth sample in the figure has been rotated in the ac-plane where the orientations are as noted in the figure caption. There are several consistencies to the measurements which are important to note. First, in cases where the field is aligned with the conducting axis (B // b), the magnetoresistance drops monotonically for all samples to a value which remains nearly constant to the high field limit. Second, as the samples were rotated away from this orientation, the high field resistance increased, in some cases making a large upturn. The a-axis is the second most conducting direction of the unit cell, making the B // c-axis orientation the most likely orientation for orbital motion to take place. In figs. 5.3.6a – 5.3.6d, the CDW state is more resistant to suppression in this orientation, which can be attributed to an orbital contribution to the magnetoresistance. From figure 5.2.2, magnetic fields of 33 tesla are not large enough to close the energy gap. Judging “by eye” from Fig 5.2.6, when the field is parallel to the b-axis we estimate that the gap is completely closed by fields closer to ~ 36 tesla.
Figure 5.2.6. Angular dependence of (Per)$_2$Au(mnt)$_2$. Samples in (a) – (c) were rotated from $\theta = 0^\circ$ ($B // b$) to $\theta = 90^\circ$ ($B // c$) using currents of 10 $\mu$A [(a) and (b)] and 1 $\mu$A. For (a) and (b) The unmarked orientations are 13$^\circ$, 27$^\circ$, 41$^\circ$, 55$^\circ$, 69$^\circ$, and 83$^\circ$. The sample in panel (d) was rotated from $B // a$ ($\phi = 0^\circ$) to $B // c$ ($\phi = 90^\circ$). Angles not indicated are 17.5$^\circ$, 35$^\circ$, 52.5$^\circ$, 70$^\circ$, and 87.5$^\circ$. 
Figure 5.2.7. The derivative of the logarithm resistance with respect to inverse temperature is shown at different constant magnetic fields. The arrows show where the transition temperature is defined for the metal-CDW phase boundary. Inset: Temperature curves where the transition temperature is indicated by the solid arrows and the resistance minimum is shown by dotted arrows.

Figure 5.2.7 shows the derivatives of the natural logarithm of the cooling curves plotted versus inverse temperature. The peaks (marked with arrows in the figure) are used to define the transition temperature. In higher fields where the CDW is almost completely suppressed, the transition temperature becomes increasingly difficult to measure. In the inset to figure 5.2.7, the transition temperatures from cooling curves at zero field, 20 T, and 29 T are shown by the solid
arrows. The dotted arrows show the resistance minima preceding the metal-insulator transition. With increasing fields these value shift in opposite directions.

Figure 5.2.8. Transition temperature v. magnetic field phase diagram for (Per)$_2$Au(mnt)$_2$. The measured energy gap v. field is shown using the right axis. Error bars are defined by the width of the Gaussian used to determine the peak locations in Fig. 5.2.7. The transition temperature and energy gap are normalized to values of 11.3 K and 83 K, respectively.

The phase boundaries defined by the derivatives of samples in the B // b and B ⊥ b orientation are shown in the temperature-field phase diagram (Fig. 5.2.8). The transition temperature for the parallel field alignment has been fit to the behavior predicted in the work of Dietrich and Fulde using equation 2.2.10. The value of 0.148 for $\gamma/4$ is lower than expected but consistent with results from Bonfait and Matos at high fields [33,34]. A projection of the data for $\Delta_{CDW}/\Delta_{CDW}(0)$ to zero provides a critical field of 35 tesla to completely close the energy gap. Using measured transition temperatures for the B // b orientation, it appears $T_{CDW}/T_{CDW}(0)$ would approach zero at a critical field 40 tesla. Both values are slightly higher than the value measured from Fig. 5.2.6. For this B ⊥ b orientation this value would be even larger but the
magnetoresistance data shows that a complete suppression of the insulating state is unlikely to occur at all. Though analogies have been drawn with BCS behavior, the zero field gap is almost four times the value calculated from $\Delta = 1.76 k_B T_c$. [83]

Figure 5.2.9. Magnetoresistance of (Per)$_2$Au(mnt)$_2$ at $T = 0.45$ K normalized to the value measured at $B = 0$ T.

All of the measurements described thus far were completed in dc fields. The magnetoresistance in figure 5.2.9 was measured using a constant dc current source and the voltage was recorded using a digitizer. The results are consistent with the measurements in dc fields to 45 tesla. The magnetoresistance in the $B \perp b$-axis orientation continues to increase to the maximum field value. In light of the field-induced density wave state of $M = Pt$, discussed in the following section, we may predict that a similar state occurs in fields of 70 – 80 tesla.
5.3 (Per)$_2$Pt(mnt)$_2$

The 12 K transition temperature of M = Au and the BCS relation $\Delta_o = 1.76k_BT_c$, give an expected energy gap of around 21 K. This value can be used to determine the Pauli (Clogston) limit,

$$B_P = \frac{\Delta_o}{\sqrt{2}\mu_B}$$

of a superconductor at which Cooper pairs are broken and superconducting materials become metallic. The energy gap estimated for M = Au gives a Pauli critical field of 22 T where, assuming the gap of the CDW state follows similar behavior to a BCS system, the CDW should be suppressed. The experimentally measured energy gap measured from the Arrhenius plot of fig 5.2 between 5 – 10 K was approximately 86 K. This provides a Pauli limit of ~ 90 tesla, which is above experimentally achievable fields. In section 5.3, magnetostriction measurements showed that an applied field of ~ 36 T suppresses the CDW state of (Per)$_2$Au(mnt)$_2$, in the B // b orientation.

Figure 5.3.1. Zero field cooling curves for two M = Pt samples. Thick, dotted lines show the temperature range where the value of energy gap was found. Inset: The resistance v. temperature curve.
The temperature dependence of two $M = \text{Pt}$ samples is shown in figure 5.3.1. Both samples have a resistance minimum at approximately 15 K. The resistance increases very quickly when the temperature is lowered further to 7.1 K. Analysis by a derivative plot for ln(resistance) shows a maximum to define the transition temperature at 6.9 K. It is clear in the figure that the $M = \text{Pt}$ materials, similar to $M = \text{Au}$ do not follow a simple BCS behavior. Instead, large energy gaps near $\sim 300$ K are measured from temperatures below the phase transition. The slope is not constant and can be fit in a second, lower temperature regime which results in smaller energy gaps. It is unlikely that the change in slope occurs from depinning effects in this case. The threshold field for $M = \text{Pt}$ was measured by Lopes, et al. at $T = 4.2\text{K}$, where a value of $8.9\text{V/cm}$ was found. [87] These two samples in figure 5.4.1 were measured with 1 $\mu\text{A}$ of current so even a measured voltage of 100 mV would only correspond to 100 nW of heating power. A temperature dependence for $M = \text{Pt}$ with two distinct temperature regions below the transition temperature has been observed in previous measurements.

![Figure 5.3.2. Magnetoresistance of (Per)$_2\text{Pt(mnt)}_2$ in the orientation B // c-axis.](image-url)

80
The suppression of the CDW by the application of a magnetic field is a competition between energies. Following expected BCS behavior once again for a system with an energy gap, we can expect a Pauli limiting field of about 15 tesla. Using the measured gaps (~300 K) from figure 5.3.1 to provide a prediction, an applied magnetic field of 320 tesla would be necessary to suppress the CDW state. The lower temperature

Considering the ratio of transition temperatures for \((M=\text{Au})/(M=\text{Pt}) \rightarrow 3:2\), one might expect the critical magnetic field to follow the same ratio. As shown in the Fig. 5.3.2, the conventional, low field CDW (henceforth, referred to as CDW\(_o\)) is suppressed in a field of ~24 T, following the expected 3:2 ratio. Note that part of the each of the magnetoresistance curves for temperature 0.5 – 3.5 K, has been removed at lower fields. In this region the sample has such a high resistance that the applied current goes to zero and the sample cannot be measured by a lock-in amplifier. At each temperature the magnetoreistance goes through a minimum near 24 T, which is progressively wider at higher temperatures. This resistance minimum can be considered metallic below 1K, but shows activated behavior for higher temperatures. The magnetoresistance at \(T = 0.5\) K dropped to an unreadable value for the lowest temperature measurement. The onset of a second density wave state is observed in fields beyond 24 T as the resistance quickly increases. During this rise in resistance, steps or a “cascade” is observed at the lowest temperatures. A plateau appears at ~33 T, which does not shift to higher or lower fields with changing temperature. Near 37 T, the resistance once again begins to drop but is an activated semi-conductor in the high field region.
The temperature dependence of the magnetoresistance of a second M = Pt sample is shown in figure 5.3.3 for the magnetic field aligned with the conducting axis. The CDW₀ state is suppressed in nearly the same field, labeled B₀, as in the B // c-axis orientation. The intermediate lower resistance region is broader, followed by an increase in magnetoresistance at 35 T (Bₓ) into the field-induced density wave state. In this orientation the high field state is centered around 40 T. A decrease in resistance is observed towards the high field limit. Features observed in the magnetoresistance above Bₓ have been labeled Bₐ – Bₜ. The high field density wave behavior for the B // c orientation was easily observed at a temperature of 4.2K, whereas the same temperature produces a flat magnetoresistance in high fields in figure 5.3.3. The step-like behavior during the resistance increase is not as pronounce in the B // b-axis orientation, but this could be due to sample dependence.
Mounting a M = Pt single crystal on the sample platform of a rotation probe allowed for measurements of all angles between the two orientations shown in figures 5.3.2 and 5.3.3. The critical field at which the CDW₀ state is suppressed is nearly isotropic in comparison to the transition to the FIDW state. The B // b (θ = 0°) transition field is 2 tesla higher than for the θ = 84° orientation (nearly B // c). As the angle between the applied magnetic field and the conducting axis decreases, the low resistance state broadens and the magnetoresistance becomes negative in this region. These results are consistent with what was observed for B // b. With the field nearly perpendicular to the b-axis (B // c), the low resistance region is narrows but not to the amount observed in figure 5.3.2. The onset of the FIDW state shifts ~ 5.5 tesla towards higher fields when the sample is rotated from B // c to B // b. The feature labeled B₀ in figure 5.3.3 is observed again in the magnetoresistance of figure 5.3.4 before the resistance plateau of the FIDW state. As mentioned in section 5.1, the calculated transfer integrals are by far largest in
the $b$ direction but electronic bandwidth also exists in the $a$ direction. Hence, in the B // $c$ orientation there is a possibility of orbital motion for the charge carriers, which seems to drive the FIDW state to lower fields.

![Magnetoresistance data](image)

**Figure 5.3.5.** Magnetoresistance data for M = Pt at $T = 0.5$ K using dc measurement technique in B // $c$ orientation. Inset: Cooling curve for the same sample (red curve). The dotted line shows the same curve with 0.1 $\mu$V added to the signal.

The magnetoresistance observed from the B // $c$ orientation in figure 5.3.2 shows a strongly activated region of lower resistance between the CDW$_o$ and FIDW states. Below 1K, a drop in resistance to a small, negative value is observed. The inset to figure 5.3.5 shows a zero-field cooling curve for a sample of (Per)$_2$Pt(mnt)$_2$ (red curve). Between 16 and 37 K, the resistance is measured as a small, negative value. With a 0.1 $\mu$V offset added to the data a typical cooling curve (with positive values) is restored. The reasoning behind these decreases in resistance below zero is elusive. Magnetoresistance behavior similar to figure 5.3.2 was observed for another M = Pt sample measured with an oscillating dc current (500 ms. steps for +/- current). With a small current of only 10 nA we find that the magnetoresistance becomes negative in the range 24 to 34 tesla. Increased currents narrow this range as shown in figure 5.3.5. With an
applied current of 50 \( \mu \text{A} \) the signal is positive is this region. The larger currents also serve to decrease the magnetoresistance in the CDW\(_{\sigma}\) state where larger current values produce a depinning electric field across the sample. The most likely explanation for the cooling curve and magnetoresistance behavior is just a steep decrease in resistance where the conduction paths through the material are changed, but not truly negative. In the lower resistance region, typical sample resistances are in the range of hundreds of ohms (see figure 5.3.4).

Figure 5.3.6. The second derivative of the magnetization of (Per)\(_2\)Pt(mnt)\(_2\). The arrows point out the peaks in the data. The dotted red lines are magnetoresistance data with the same orientation as the nearby magnetization curves.

A small sample (mass < 100 \( \mu \text{g} \)) was attached to the sample arm of a PRC120 cantilever, which was mounted to the sample platform of a rotation probe. The rotation occurs in the \( ac\)-plane and we define the orientation \( B // c \) as \( \theta = 0^\circ \) (\( B // a \) corresponds to \( \theta = 90^\circ \)). The platform
was rotated in ~ 7° increments and the magnetic field was swept at each angle. The data shown in figure 5.3.6 is the second derivative (curvature) of the magnetization data. Two peaks are observed in each upsweep (peaks 1 and 2). Speculation as to the origin of the changes in magnetization may suggest they are produced by the de Haas van Alphen effect. In the orientation B // c it is possible to have small orbit pockets from imperfect nesting of the Q1D Fermi surface. A couple of key points immediately prove this to be impossible. The raw data (not shown) contains two curvature changes which produce the peaks shown in the figure, but the peaks are not a periodic in inverse field, as is the case with quantum oscillations. Further, when an applied magnetic field is rotated away from the normal of a closed electron orbit, the frequency of the peaks increase according to 1/cos(θ). The peaks shown in figure 5.3.6 decrease in amplitude near 90°, but they are easily seen within 15 degrees of this orientation. The peaks also disappear at the θ = 0° position, where one would expect the peaks of largest amplitude for quantum oscillations. The locations of the peaks are interpreted as a signature of the phase transition. The first set of peaks (1) result from the transition from CDW₀ to the metallic state (red shading). The second set of peaks (2) results from the onset of the FIDW state (blue shading). Magnetoresistance data is plotted from the same orientations is plotted over the top of the B // a and B // c data in the figure, showing the correspondence between the two measurements.

The phase diagram for the M = Pt system in shown in figure 5.3.7. The dashed lines estimate the phase boundary between the measured zero field transition temperature and the suppression of the CDW₀ state. The FIDW phases shown in the figure are points in the magnetoresistance data which show features (peaks and valleys). The intermediate phase between the CDW₀ state and FIDW is simply referred to as the lower resistance region. At these fields there is still strong activation of the resistance. Metallic behavior and even resistance too low to be measured has occurred in the B // c orientation for isolated cases. Near the high field limit we find a strongly activated region. The magnetoresistance drops from the FIDW to this region but the behavior is more activated than the LR area of the phase diagram.

Extrapolating data from the phase diagram of M = Au, an applied field of ~ 36 tesla is necessary to close the energy gap. Comparing the energy scales of the M = Au and M = Pt materials from the transition temperatures (12 K and 8 K, respectively), a critical field of ~ 24 tesla was expected. As the phase diagram shows (fig. 5.3.7), the CDW₀ state follows this
prediction closely for both orientations shown. More measurements are needed for a full description of the higher field density wave state.

Figure 5.3.7. The temperature-magnetic field phase diagram for (Per)$_2$Pt(mnt)$_3$ in the (a) B // b and (b) B // c orientations. The dashed line represents the likely phase boundary between CDW$_o$ and the metallic state. Filled (open) symbols represent features below (above) the FIDW state. LR = lower resistance region.
5.4 Pressure Dependence of $M =$ Au, Pt

The cooling curves shown in figure 5.4.1a show the change in sample resistance for $M =$ Au under quasi-hydrostatic pressure in a BeCu pressure cell. At the lowest temperature measured all of the resistances drop with increasing pressure. In the inset to figure 5.4.1a the resistance minima, which precede the metal-insulator transition at higher temperatures, are plotted versus...
applied pressure. In contrast to the sample resistance at base temperature, the resistance minima appear at decreasing values of temperature with increasing resistance until 4.5 kbar. The values then shift to higher temperatures as further pressure is applied, in agreement with previous estimates. [28] The temperature dependence of the \( M = \text{Pt} \) sample at 2.2 kbar shows a monotonic increase in resistance in the measured temperature range (fig. 5.4.1b). An upturn in resistance is observed in the cooling curve near 5 K, which is below the transition temperature of 8 K measured for ambient pressure samples. The higher temperature resistance metallic region shows only a small decrease in resistance for the five pressures measured. Under the influence of 2.2 or 3.3 kbar of pressure, the CDW\(_0\) ground state is still observed in the \( M = \text{Pt} \) sample by the high resistance at low temperatures. Higher pressures decrease the sample resistance to a value which is almost constant over the measured range. The highest applied pressure produces a decrease in resistance at the lowest temperature.

Figure 5.4.2. Transition temperature versus applied pressure phase diagram for \((\text{Per})_2\text{Au(mnt)}_2\). Red circles and blue triangles indicate two different measured samples. \( T_c \) was taken from the peaks of derivative logarithm plots.

Data traces must be clean and free of signal noise to extract the transition temperature from peaks of \( d(\ln(R)/d(1/T)) \). Without clean data, the differentiated data can be difficult to
interpret. The temperature dependence data of high enough quality for this analysis was measured for two samples of $M = \text{Au}$. The transition temperatures for both samples, normalized to transition temperature at 2 kbar, are shown in figure 5.4.2. A Gaussian fit (dotted black line) of the data from both samples finds a minimum occurs near 5.5 kbar, similar to what is observed with the analysis of the resistance minima in the previous figure.

In general, pressure affects a crystal lattice in several ways. First, the lattice parameters of the crystal are changed with pressure, depending on the distances and interactions between the molecules. Second, the overlap of the molecular orbitals extending from the donor molecules increases. This produces a larger bandwidth in all directions. It is possible to observe this directly as the resistance decreases with added pressure in almost all cases. The dimensionality of the system increases as the Fermi surface becomes increasingly warped for a Q1D material. The nesting condition becomes more complex. With the above changes the Brillouin zone must be redefined.

Qualitatively speaking, pressure gives the electrons more translational degrees of freedom so they are not restricted to 1D motion. This is due to a stronger interchain hopping in the $a$-direction (and probably to a lesser degree, in the $c$-direction), which drives the system more two-dimensional. Though a transition temperature can still be measured under the influence of pressure, the magnetoresistance data suggests the material might become a Q2D metal.
The magnetoresistance of one single crystal of M = Au is shown in figure 5.4.3 under the influence of four different pressures. As mentioned, in cases where the data begins at 11.5 tesla, the superconducting outsert magnet of the hybrid magnet system was at maximum field before the resistive insert was swept in the range 11.5 – 45 tesla. With 2.2 kbar of pressure we see a sample resistance is measured in tens of ohms rather than kohms, as is the case with ambient pressure measurements. The slope of the lower field magnetoresistance indicates that the CDW₀ state persists under this value of pressure. A minimum is observed at 24 tesla before the resistance rises to the high field limit. At 4.1 kbar the overall resistance drops, as expected, and the effects of the CDW₀ state are diminished further. The minimum in the magnetoresistance shifts slightly to higher fields (~ 25 T) before the resistance rises during the remaining upsweep. A zero-field resistance of only 300 mW is seen with 6.0 kbar of pressure, indicating that the influence of the CDW₀ state cannot be resolved. The magnetoresistance rises to a peak near 20
tesla, shows a drop to a minimum at 30 tesla and rises as with the previous measurements (the limiting field for this measurement was 33 tesla). Interestingly, a higher pressure shows a slight increase in resistance at low fields. This is consistent with the temperature-pressure (TP) phase diagram which suggests pressures near 5.5 – 6.0 best suppress the CDW\textsubscript{o} state. It is difficult to estimate between the TP phase diagram and the magnetoresistance under pressure if the CDW\textsubscript{o} state still exists.

![Graph showing magnetoresistance](image)

**Figure 5.4.4.** Magnetoresistance of M = Au under P = 4.1 kbar (left-axis) and 6.0 kbar (right-axis) of pressure showing SdH-like behavior. Inset: At 6.0 kbar of pressure the material shows metallic behavior at low fields.

The contacts of the sample measured for figure 5.4.4 were configured to measure the Hall effect across the \(a\)-axis of the sample. A true Hall effect measurement must be measured in positive and negative fields so the effects of longitudinal resistance can be cancelled. The contacts in this configuration are never perfectly aligned in the transverse direction, therefore the \(b\)-axis signal (due to the high conductivity) dominates the signal. Hence, we show the magnetoresistance of the sample as a measure of the \(b\)-axis. The lower pressure measurement
(4.1 kbar) shows a peak near 14 T, followed by a resistance minimum near 20 T. This is consistent with the data shown in figure 5.4.3. In contrast to the previous figure the magnetoresistance of this sample reaches a maximum near 38 tesla for the lowest two temperatures measured. Data taken at a higher pressure (6.0 kbar) also shows some interesting features. First, the magnetoresistance at the lowest fields shows metallic rather than activated behavior (inset to figure 5.4.4). As the field is increased, peaks are observed in the magnetoresistance at approximately 6.5, 9 and 15 tesla before rising to the maximum field. The area of the orbital area is periodic in inverse field so by calculating the inverse difference of the values of adjacent peaks using

\[ \text{Frequency} = \left( \frac{1}{B_2} - \frac{1}{B_1} \right)^{-1} \]  

(Eq. 5.4.1)

we find a frequency value of \(~22\) T. A one-dimensional Fermi surface cannot produce closed orbits so another explanation is required. The addition of pressure can warp a Q1D Fermi surface in the manner shown in figure 2.2.3. The proper nesting vector can overlap pieces of the Fermi surface while still leaving open pockets which produce closed orbits when a field is applied.

![Graph](image)

Figure 5.4.5. Magnetoresistance of \((\text{Per})_2\text{Au(mnt)}_2\) under 5.0 kbar of pressure at \(T = 0.5\) K. Inset: The range of field indicated by the red arrows has been expanded for the inset, with the background subtraction.
A second sample shows this behavior more clearly in figure 5.4.5. A pressure of 5.0 kbar produces a zero-field resistance on the order of hundreds of milliohms. As the field is increased a rapid rise in magnetoresistance is observed. Above 5 T, clear peaks begin to appear in the data followed by a broad minimum at 22 T. The sample resistance rises, as in previous cases to the high field limit. A closer look at the low field range of the magnetoresistance reveals peaks which are resolvable as low as 3 T. A linear fit was made to the 3 – 5 T background magnetoresistance and then subtracted. The resulting peaks are shown in the inset to figure 5.4.5.

A fast Fourier transform of the data produces a broad peak at 18.2 tesla but with the limited number of peaks, the accuracy is questionable. Instead, we use the differences in inverse field values as we did with figure 5.4.4. The average of the frequencies is 21.5 T. The oscillations have a substantial background which must be subtracted before the amplitude of the peaks can be fit with the $R_T$ damping parameter (Eq. 2.1.9). The resulting effective mass is $\sim 0.4m_e$, indicating metallic behavior despite the background magnetoresistance.

Figure 5.4.6. The indexed oscillations peaks 1 – 6 versus inverse field. A linear fit shows the y-intercept is near $n = -\frac{1}{2}$.
For quantum oscillations the Landau levels are indexed from \( n = \infty \) at low fields. Of course we cannot realize these peaks experimentally. In chapter 4, the orbital frequency of \( \tau \)-EDO was \(~ 50\, \text{T}\) so the final measured peak was the \( n = 1 \) peak. The peaks of figure 5.4.5 are labeled from 1 – 6 with the peak near 15 T used as \( n = 1 \). The indices are plotted versus inverse field in figure 5.4.7. The peaks from figure 5.4.6 clearly ride on a background resistance which does not follow the Lifshitz Kosevich formula yet the peaks are still linear with respect to the inverse magnetic field.

Quantum oscillations frequencies are most easily determined using a FFT, which measure the amplitude of the most prominent frequencies within a wave. In cases such as the pyrazino tau material, with a frequency of \(~ 500\, \text{T}\), a number of oscillation peaks are observed within the range of the applied field. The estimated orbit frequency observed in the \( M = \text{Au} \) system under pressure suggests an orbit of \(~ 20\, \text{T}\) as measured from the difference of neighboring peak values. Oscillations are first observed following the partial suppression of the \( \text{CDW}_0 \) state near 4 kbar.

**Figure 5.4.7.** – Changes in oscillation frequency with increasing pressure. The lowest frequencies used (blue circles) were taken only from the final peak positions of the magnetoresistance. The other values were taken from subtracting the \( n = 1 \) and \( n = 2 \) peaks.

Average change in frequency is \( \Delta \text{Freq} = 0.972\, \text{T/kbar} \).
Also zero-field resistance also reaches a minimum near this pressure. Oscillations frequencies observed under a range of pressures from 4.0 – 8.3 kbar are noted above for four samples. The value of the frequency in each case in found from Eq. 5.4.1. The value of the frequency shifts to higher fields is all cases at a rate of ~ 0.972 T / kbar. The closed orbits most likely come from imperfect nesting of the Q1D Fermi surface. Increasing pressure creates a larger orbital area in k-space by warping the Fermi surface, which decreases nesting.

Figure 5.4.8. Angular dependence of magnetoresistance of (Per)$_2$Pt(mnt)$_2$ under 6.2 kbar of pressure (T = 270 mK). Dotted lines represent B // c and B // -c. $\theta = 0^\circ$ corresponds to B // c, $\theta = 90^\circ$ corresponds to B // a and $\theta = 180^\circ$ corresponds to B // -c. Data is offset for clarity and plotted sequentially between the given orientations.
Because of the experimental volume of the cryostat for high field measurements is too small, rotation of the pressure cell is not possible. A shortened BeCu pressure cell made it possible to rotate a sample of (Per)$_2$Pt(mnt)$_2$ under 6.2 kbar of pressure in a wider bore superconducting magnet. When the field is aligned with the $c$-axis of the sample, orbital motion is possible and the behavior of the magnetoresistance suggests quantum oscillations. As mentioned above, with higher frequency oscillations, it is simple to analyze the data using a fast Fourier transform. While inspecting the angular dependence the frequency of quantum oscillations should follow $F(\theta) = F(\theta=0^\circ)/\cos(\theta)$ behavior, where $\theta$ is the angle between the applied field and the conducting plane. By eye, one can observe the features of the magnetoresistance move to higher fields with rotation from the $90^\circ$ (-90°) orientation. When the peaks are analyzed by pairs to estimate the orbit area, the frequencies are inconsistent. The lower limit of the values obtained (21 T) approximately matches the value obtained for frequency the $M = Au$ measurements. The upper limit of 34 T is far too high and occurs is found at unexpected orientations.

The same sample used for rotation under pressure was rotated to the $\theta = 0^\circ$ ($B \parallel c$) orientation where the magnetic field was swept at a number of temperatures. The magnetoresistance oscillations should grow in amplitude as the field gets larger but the peak with the larger amplitude near 8 tesla precedes a smaller peak at $\sim 14$ tesla (fig. 5.4.9). Nonetheless, fast Fourier transforms reveal a peak at 17.8 T. The amplitude of these peaks were fit the $R_T$ parameter where an effective mass of $0.6m_e$ was found, in agreement with the effective mass found for the oscillations in the $M = Au$ system.
Figure 5.4.9. Temperature dependence of the M = Pt sample from figure 5.4.8 in the B // c orientation. Pressure = 6.2 kbar. The curves were taken in the temperature listed, following the red arrow from top to bottom.
The M = Pt system was measured under applied fields to 45 tesla as shown in fig 5.4.10 in the orientation with the field aligned with the least conducting axis (B // c). For low pressures (~1 kbar) near 10 – 15 T, the magnetoresistance begins to decrease down to a minimum at 20 T, which follows the location of the low resistance state for ambient pressure measurements. The magnetoresistance increases with higher fields to a maximum around 33 tesla and then returns to an activated state at the high field limit. Interestingly, a large hysteresis is observed between the upsweep and downsweep. With larger pressures of 3.0 and 5.3 kbar, the low resistance region shifts less than one tesla to higher fields. The position of the peak (maximum point) in the high field FIDW state shifts to lower fields. As the inset to the figure shows, the hysteresis (ΔB) grows with higher pressures. Magnetoresistance measurements from zero to 17.5 tesla are shown.
by the dotted lines in the figure. The lower field data at 6.2 kbar clearly shows two peaks which have a corresponding frequency of 21.4 T. The 5.3 kbar higher field trace shows a peak near 13.5 T which matches the second peak in the lower field data. From this we can conclude that the M = Pt material also produces closed pockets from imperfect Fermi surface nesting which result in quantum oscillations. In comparison to M = Au, a coupling between the spin and conducting chains may occur in the M = Pt system. Adding pressure to a sample decreases the distances between the lattice sites which will increase the strength of interactions.

Under ambient pressure, in the B // b orientation, the FIDW state was observed but the critical fields were shifted to higher values (Fig. 5.3.2). With the application of only 1 kbar of pressure, the magnetoresistance of M = Pt in the B // b orientation does not show a FIDW state (fig. 5.4.11). The magnetoresistance monotonically decreases from 11.5 T to the high field limit. This behavior is repeated at a higher pressure of 3 kbar. At 5.3 kbar, a positive magnetoresistance is observed to ~ 20 T before following the same high field behavior as the two lower pressures. The upsweep and downsweep traces are shown for all three pressures though they are difficult to distinguish. The data overlaps completely without any hysteresis. A second sample was measured in lower fields between zero and 17.5 tesla. With a pressure of 2.2 kbar the magnetoresistance decreases with field as the effect of the CDW_0 state is decreased. A higher pressure of 6.6 kbar shows a positive magnetoresistance over the entire range of field measured.
Figure 5.4.11. Magnetoresistance of (Per)$_2$Pt(mnt)$_2$ in the B $\parallel b$-axis orientation at $T = 0.5$ K. The data at 2.2 and 6.6 kbar (red traces) is from a different sample than the other three traces (black, blue and green). Lower field measurements (dotted lines) were multiplied by a value between 0.1 – 1 to match resistances with the higher field measurements.
5.5 Conclusions and Discussion

The transition temperature of \((\text{Per})_2\text{Au(mnt)}_2\) decreases as a function of the applied magnetic field. In the B // b-axis orientation, the change in transition temperature can be fit to a dependence on the square of the field, but with a prefactor smaller than predicted. High field measurements also show that the magnetoresistance decreases monotonically to a critical field of \(\sim 36\) tesla where it becomes nearly constant. Values of \(\Delta/k_B T\) are found to be \(5 - 10\) from the zero-field temperature dependence of the M = Au system and about five times larger still for M = Pt, in contrast to the mean field value of 1.76. Mean field theory estimates are based on a one-dimensional do not take into account the small, but finite, transverse bandwidth \((t_a)\) and must be modified in the limit where \(k_B T_c \sim \mu_B B\). The magnetoresistance behavior of \((\text{Per})_2\text{Au(mnt)}_2\) in the B // c orientation suggests further consideration must be given to the description of the state where orbital mechanisms become involved.

The critical field of \(36\) tesla for M = Au (B // b orientation) is in complete agreement with a value of \(24\) tesla for M = Pt, based on the 12 K / 8 K ratio of transition temperatures for the two materials. The higher field density wave state behavior for M = Pt was unexpected. Zanchi et al. have predicted high field states which could exist as a hybrid of a CDW and SDW (called CDW\(_x\)). As in the case of FISDW states, the nesting vector varies as a function of the magnetic field but also takes into account the degree of charge and spin ordering in the material. We have observed the critical field \((B_o)\) which suppresses the conventional CDW\(_o\) state as well as a second threshold field \((B_x)\) which induced the high field state, CDW\(_x\). Another high field state is predicted (CDW\(_y\)), which is dependent on the angle between the field and the a-axis (in the ac-plane). A difference between B // c and B // a orientations is observed in the onset to the FIDW state but it is more angular dependence measurements are needed before a critical angle can be assigned for the CDW\(_o\) to CDW\(_y\) transition. The high field FIDW state studied for M = Pt is likely to be observed in the M = Au material in higher fields considering the rising magnetoresistance which is observed towards the high field limit in the B // c orientation.

Figure 2.2.4 is repeated here for comparison with our results for the phase diagram of M = Au to 33 tesla. Note the reduced field axis where \(B \rightarrow (\mu_B B)/(k_B 2\pi T_c)\), where we have used our measured \(T_c\) of 11.3 K. The M = Au results for ambient pressure are above the perfectly nested limit of the phase diagram, taken from figure 9 of reference 52.
The ZBM phase diagram is dependent on the strength of the nesting condition for the 1D Fermi surface. This can quantitatively be estimated by

\[
\frac{t_y'}{t_y'^*} \approx \frac{t_y'}{T_c(t_y = 0)}
\]

where \(t_y'\) is the antinesting parameter and \(t_y'^*\) is the value of the antinesting parameter which would suppress the CDW in the absence of a magnetic field (from section 2.2.6). At ambient pressure, the ratio \(\frac{t_y'}{t_y'^*} \sim 0.038\) predicts the system will be nearly perfectly nested. The transverse and longitudinal bandwidths (\(t_a\) and \(t_b\), respectively) both become larger with applied pressure. The transition temperature also changes with pressure and at 5.0 kbar is nearly 50% of the ambient pressure value. Depending on the ratio of these changes the imperfect nesting parameter may quickly grow to \(\sim 1\). The ZBM phase diagram predicts the transition temperature will rise as...
a function of magnetic field with these conditions. Several measurements of high field temperature dependence agree with this prediction but more measurements are necessary.

The transition temperature of $M = \text{Au}$ is suppressed, but only to a pressure of $5 - 6 \text{ kbar}$ before it rises again with larger pressures. Our results agree with reference 28 where a $T_c$ minimum is also found under $\sim 6 \text{ kbar}$ of pressure for $M = \text{Au}$ and $M = \text{Pt}$. (Our transition temperatures for $M = \text{Pt}$ were inconclusive as no $T_c$ or resistance minimum were observed in the temperature dependence). Pressures of greater than $4 \text{ kbar}$ produce a small pocket from imperfect Fermi surface nesting, as observed through Shubnikov de Haas oscillations. The pocket increases in area at higher pressures which produces larger frequencies. The overall magnetoresistance does not follow the Lifshitz Kosevich formula which provides a flat background for quantum oscillations. This calls into question if the oscillations are Shunikov de Haas oscillations or a cascade of phase transitions. In a FISDW state, where this type of behavior is observed, an applied field of several tesla is necessary before the nesting condition is met and the system enters the first FISDW state. By indexing our oscillation peaks we observe the oscillations can be extrapolated back to zero field where a closed orbit is first quantized, suggesting we do see SdH oscillations.

The band structure and Fermi surface calculations of Canadell et al., [84] provide a second possibility as to the origin of the closed orbits. The Perylene donors are tilted with respect to the $b$-axis within each conducting chain. The four donor stacks of the unit cell contain molecules which are tilted in different orientations. Due to this asymmetry, four Fermi surface sheets rather than one lie in very close proximity at the points $+/_- k_F$ along the $k_b$-axis. If this description is accurate, then the closed orbit pockets observed under pressure may result from these sheets. A critical pressure of 4 kbar may be enough to push the sheets close enough so they touch. The frequency of the oscillation in all cases is found to be approximately 20 tesla. This suggests that the rising high field resistance following the $n = 1$ oscillation peak is the quantum limit, where system has developed an energy gap after the final Landau level passes the Fermi level.

By applying pressure a 2D conducting plane is created. The indexing of the SdH peaks provokes an interesting possibility. The six resolvable peaks of the magnetoresistance of figure 5.4.5 can be counted for $n = 1$ to $n = 6$ with the $n = 1$ peak at $\sim 15 \text{ T}$. Using these values a fraction $n = 1/3$ state would occur at a field value of 45 tesla. Further transport measurements are
necessary under pressure using a dilution refrigerator to check if this peak can be more clearly resolved.
CHAPTER 6
SUMMARY AND CONCLUSIONS

The tau-phase two-dimensional materials have been studied with a number of measurements to determine the origin of the high field metal-insulator transition. Magnetoresistance measurements have produced consistent results confirming that transport becomes impossible at high fields. A complimentary measurement of thermopower confirms that a rapidly increasing energy gap is produced in high fields, which localizes the charge carriers. The weak angular dependence of the system shows that the transition does not require an orbital mechanism.

Differences in the high field results for between the $\tau$-(P-(S,S)-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ and $\tau$-(EDO-(S,S)-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ materials prove the importance of stoichiometry in producing the insulating state. Studies of the quantum oscillations for these materials have proven that there are differences in the Fermi surface. The pyrazino system follows a model of a loosely bound lattice with an instability against a field-induced distortion. Application of the relatively small pressure $\sim$ 1 kbar completely suppresses the high field insulating state, revealing Fermiology results consistent with lower field measurements. Magnetization results clearly follow the large hysteresis of magnetotransport at ambient pressure, providing further evidence of a mechanism which couples the lattice to the field beyond 35 tesla.

Further measurements of the tau systems would focus on the lattice of the system. Measuring transport under strain may drive the metal-insulator transition to lower fields. Measuring the lattice structure at low temperatures and in high fields may some day be possible.

High field studies of the quasi-one-dimensional materials, (Per)$_2$Au(mnt)$_2$ and (Per)$_2$Pt(mnt)$_2$ proved that mean field estimates are inadequate for predicting high field behavior. The suppression of the energy gap for the M = Au system in the B || b orientation approximately follows the expected field dependence proportional to $B^2$. With the field perpendicular to the chains similar behavior is observed to $\sim$ 35 tesla where magnetoresistance rises. The transverse bandwidth of these materials is small but enough to create orbital effects.

With a transition temperature of only 8K, the low field charge density wave of M = Pt is suppressed in a field of 25 T, following the same behavior as M = Au. A field-induced density
wave state is observed at fields between 30 and 40 tesla. This state has been identified as a hybrid of CDW and SDW states made possible made a nesting vector which is modified by high fields. By applying pressure to the perylene materials we were able to suppress the conventional low field CDW state. In magnetic fields oscillations are observed with follow periodicity of Shubnikov de Haas oscillations but have a large background resistance. The low frequency of the oscillations (~20 T) makes is possible to reach the quantum limit.

Preliminary $^{195}$Pt NMR measurements have not been conclusive due to the low natural abundance of this isotope and its overall low concentration in the structure. Measurements on larger samples in the field region of the FIDW state will investigate the role that the Pt spins play in creating this state.
APPENDIX A
PIEZORESISTIVE CANTILEVERS

A.1.1 Piezoresistive Cantilever Used as a Torque Magnetometer

A torque magnetometer uses a homogenous magnetic field to measure the torque created by transverse magnetization following the formula,

$$\vec{\tau} = \vec{M} \times \vec{B}.$$ 

A perfect alignment of field and magnetic moments will produce no torque. In contrast, force magnetometers use a magnetic field gradient to produce a force,

$$\vec{F} = \vec{\nabla} (\vec{M} \cdot \vec{B}).$$

This method could also be used with the cantilevers in a well-calibrated magnet by lowering or raising the sample and cantilever by a known value from the center of the magnetic field. This appendix describes measurements solely using the former method.

![Diagram of the entire assembly and a more accurate drawing of the sample and reference cantilever arms with piezoresistors](image)

Figure A.1.1. (a) Cartoon of the entire assembly. A representation of the sample of the arm is shown larger with dimensions. (b) A more accurate drawing of the sample and reference cantilever arms. The red arrows points to the piezoresistors (grey areas) of the cantilever arms.

Piezoresistive cantilevers were introduced as a miniature torque magnetometer in Chapter 3. The design of these devices has not changed a great deal since their inception in 1993. [91] The cantilevers (schematic shown in Fig A.1.1a), are produced with n-type Si wafer substrate.
During the fabrication process, the piezoresistive portions of the cantilever assembly (grey areas of figure A.1.1b) are produced by boron ion implantation followed by thermal dopant activation. The circuit paths of both arms of the cantilever include the piezoresistors, which change resistance values as strain is applied.

Though originally designed for use with atomic force microscopes, the cantilevers have shown a surprising versatility. The high sensitivity of the devices led Rossel, et al., [93] to use them to measure the superconducting transition behavior of the cuprates, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{Hg}_2\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{10}$ in dc fields. Ohmichi and Osada [61] proved that this technique could also be used in pulsed fields while measuring the de Haas van Alphen effect of $\alpha-(\text{BEDT-TTF})_2\text{KHg(SCN)}_4$ with a rise time of only 15 ms.

Previous Fermi surface measurements have given values of approximately 650 T for the area of the closed orbits with a field applied perpendicular to the $ab$-conducting plane. [94] Figure A.1.2 shows de Haas van Alphen (dHvA) oscillations in the magnetization signal for a sample of the $\lambda$-BETS material with $x = 0.6$. The orientation between the applied field and the
$ab$-plane is $\theta = 50^\circ$ and a frequency of 1007 tesla is found from a FFT of the data. Taking the orientation into consideration, the measured frequency value agrees well with previous measurements ($F = 1007 \ T \cos(50^\circ) = 647 \ T$). Perhaps more interesting than the measurement of the quantum oscillations is the observation of lower field phase transitions (inset to figure A.1.2).

The phase diagram of quasi-two-dimensional organic material, $\lambda$-(BETS)$_2$Fe$_x$Ga$_{1-x}$Cl$_4$ ($x = 0$ to 1), shows a superconducting ground state for the $x = 0$ alloy. [95] As the value of $x$ is increased, the ground state becomes antiferromagnetic (AFM). As a field is applied, a phase transition is observed near 1 tesla which corresponds to a spin-flop transition as the low temperature AFM ordering becomes tilted. This canted AFM state remains to fields of $\sim 7.1$ tesla were a metal-insulator transition has been observed in previous resistivity measurements [94], when the AFM ordering is completely suppressed.

![Figure A.1.3.](image)

The de Haas van Alphen effect was also measured for a unique organic material, Ni(tmdt)$_2$, which is comprised on a single type of molecule, rather than a donor and an acceptor. The sample dimensions ($130 \times 100 \times 20 \ \mu$m$^3$) do not allow one to easily make contacts for conventional resistance measurements. Also, the mass of the sample is too small ($\sim 0.5 \ \mu$g) for a
BeCu capacitance measurement of magnetization. A sample with the dimensions described was attached to the sample arm of a cantilever and the magnetization was measured in the hybrid magnet. Using a rotation platform, as mentioned in chapter 3, the changing magnetization was studied as a function of angle. The dHvA signal is shown in figure A.1.3 with the FFT (lower inset). The periodicity of the oscillations can be seen with the data plotted versus inverse field (upper inset). The Fermi surface calculated from the measured frequencies closely matched theoretical predictions of the three-dimensional Fermi surface. [64] The measurements of the magnetic transitions of the λ-BETS material as well as the Fermi surface of the small Ni(tmdt)$_2$ compound clearly show the versatility of this magnetization technique.

A.2.1 The Meissner Effect From a Lead Sample

![Graph showing the Meissner effect](image)

Figure A.2.1. The Meissner effect measured for a sample of high purity lead. The red dashed lines show the overall form of the magnetization. The inset show the bridge circuit used for the cantilever measurements.

A small, nearly cylindrical sample of high purity lead was attached to the tip of the sample arm of the cantilever using epoxy. Using an excitation voltage ($V_E$) of 0.1 V for the bridge, the signal of the
bridge circuit (between points B and C) was measured, as shown in figure A.2.1. The temperature of the measurement was 0.5 K, well below the superconducting critical temperature of lead ($T_c = 7.2$ K). For a type I superconductor, the magnetization of the sample created by the Meissner effect grows proportional to the applied field before the critical field of the material is reached (e.g. $\sim 0.08$ tesla for Pb). The critical field measured was $\sim 0.063$ tesla, which is actually the flux density. This can be converted to a field strength of 50 kA/m. The volume magnetization can then be found from,

$$M = \frac{H}{4\pi},$$

which yields a value of 4000 A/m.

The mass of the Pb sample was measured using a thermogravimetric analyzer (TGA) which allows the measurement of very small mass in a vacuum space so air currents will not affect the measurement. Using the mass (140 $\mu$g) of the sample and the density of Pb (11.37 g/cm$^3$) a volume of $1.24 \times 10^{-11}$ m$^3$ was found. The magnetic moment of the sample, in Gaussian units, is then $4.9 \times 10^{-5}$ emu. When the signal from the circuit measured by the lock-in amplifier is divided by the applied field, a value of $1270$ $\mu$V/T is found. Using the known magnetic moment of the Pb sample, the value of the ratio of (measured signal / applied field) from other magnetization measurements can be compared to provide an estimate of the magnetic moments for any sample.

In a separate measurement, wires were attached to the Au pads leading to the piezoresistive components of the sample arm of the cantilever. A two-terminal measurement of resistance was recorded while pressing down and lifting on the tip of the sample arm. The resistance of the piezoresistor increases with strain (pushing down) and decreases when compressed (lifting up). When the cantilever is incorporated into the bridge circuit, as $R_1$ or $R_s$ increase, the signal from the circuit becomes decreases. In the case of the Pb sample measured, the diamagnetism created in the superconducting state attracts the sample to the applied magnetic field. As the tip of sample arm is lowered towards the field, the value of the measured magnetization signal decreases, which is consistent with expectations for a measurement of diamagnetism.
REFERENCES

[57] The PRC120 cantilevers are produced by Seiko Instruments Inc., Head Office & Makuhari Unit 8, Nakase 1-chome, Mihama-ku, Chiba-shi, Chiba 261-8507, Japan.
BIOGRAPHICAL SKETCH

David Earl Graf

Education:
Florida State University – August 1999 – August 2005
• M. S. degree in Physics, August 2001.
Buffalo State College, Buffalo, NY
• B. S. degree in Physics, Summa Cum Laude, Fall 1998.

Academic Awards and Honors:
• Sigma Pi Sigma Honor Society – Inducted into the Physics honor society in 1999.
• David Vernon Bullough Award – Presented to the student with highest GPA in the Buffalo State College Physics department.
• Buffalo State College Physics Department Faculty Award – Given to a student, selected by the Physics faculty, based on achievement.
• Sigma Xi Scientific Research Society – Nominated for membership based on publication record.
• NSF GK-12 Fellowship – Three year position offered to selected graduate students in the College of Arts and Sciences to aide in teaching science in the Tallahassee community (2002 – present).

Teaching experience:
• Fall 1999 - Spring 2000: Taught astronomy lab (fundamentals of celestial observations)
• Fall 2002 - present: Teaching in K-8th grade classrooms in Tallahassee as part of the NSF GK-12 initiative.

Research interests:
Transport, magnetization, and pressure-dependence measurements of low-dimensional systems in ultra-high magnetic fields. Studies of Fermiology, metal-insulator transitions, and density-wave behavior in primarily organic materials.

Research experience:
• Undergraduate research in Mossbauer Spectroscopy of Ruthenium-based materials (1997).
• Summer Undergraduate Research Fellowship (SURF) program at the National Institute of Standards and Technology at Gaithersburg, MD (1998).
• Extensive work in dc fields at the NHMFL-Tallahassee in magnetoresistance, magnetization, and pressure dependent transport in low-dimensional systems, including studies of the Q2D tau-phase organic conductors (2000 – present).
• Several research visits to the NHMFL-Los Alamos for work in the pulsed magnet systems (2001 – 2003).
• Current research: Transport measurements and specifically, pressure-dependence investigating the field-induced density wave transition of the Q1D system, (Per)$_2$Pt(mnt)$_2$. 
**Presentations and Poster sessions:**

Oral presentation: “Metal-Insulator Transition at very High magnetic fields in an organic conductor” at APS March Meeting in Austin, TX in March 2003.

Poster session: “Magnetic field-induced density wave transition in a \( \tau \)-phase organic conductor” at Physical Phenomena at High Magnetic Fields IV Conference in Sante Fe, NM in October 2001.

**Recent relevant publications:**


**Full publication list:**


Reference contact information:
Professor James S. Brooks
Professor of Physics, Florida State University
Thesis advisor
CM/T Group
National High Magnetic Field Lab
Tallahassee, FL 32310

Ph: 850-644-2836
Fax: 850-644-5038
E-mail: brooks@magnet.fsu.edu

Professor Keizo Murata
Professor of Physics, Osaka City University
Research collaborator
Dept. of Material Science
Graduate School of Science
Osaka City University
3-3-138, Sugimoto, Sumiyoshi-ku,
Osaka, 558-8585 Japan

Phone: 81-(0)6-6605-2509
Fax: 81-(0)6-6690-2710
E-mail: muratak@sci.osaka-cu.ac.jp

Professor Penny Gilmer
Professor of Chemistry, Florida State University
Supervisor for teaching fellowship
Department of Chemistry and Biochemistry
Florida State University
Tallahassee, FL 32306-4390

Phone: 850-644-4026
Fax: 850-644-8281
E-mail: gilmer@chem.fsu.edu