Superconducting mixed state phase diagram of K-(BEDT-TTF)2Cu(NCS)2
by Monty Marcus Mola

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics
Montana State University

Abstract:
This dissertation explores the superconducting, mixed state phase diagram of the layered organic superconductor κ-(BEDT-TTF)2Cu(NCS)2. In particular, the melting of the quasi-two-dimensional (Q2D). vortex lattice is investigated throughout a wide range-of the available field and temperature parameter space. At moderate fields (0.01 - 2 tesla) and temperatures (1.5 - 10 kelvin), a cavity perturbation technique is used to study the Josephson plasma resonance. By investigating this phenomenon over a wide frequency, field, and temperature range, one can determine a line in the phase diagram that corresponds to either a flux lattice melting or depinning transition. For high fields (2 - 20 tesla) and low temperatures (0.025 - 0.300 kelvin) cantilever beam torque magnetometry is used to determine the melting of the Q2D flux lattice. In this regime, it is shown that this transition is due to quantum fluctuations in the positions of the vortices. From the results of these two experiments, one can piece together the mixed state phase diagram. Upon doing so, it is seen that the Q2D flux solid and vortex liquid states dominate the majority of the phase diagram.

SUPERCONDUCTING MIXED STATE PHASE DIAGRAM OF

κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

by

Monty Marcus Mola

A dissertation submitted in partial fulfillment
of the requirements for the degree

of

Doctor of Philosophy

in

Physics

MONTANA STATE UNIVERSITY
Bozeman, Montana

April 2001

APPROVAL

of a dissertation submitted by

Monty Marcus Mola

This dissertation has been read by each member of the dissertation committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Stephen O. Hill _____ 4/23/01
(Signature) Date

Approved for the Department of Physics

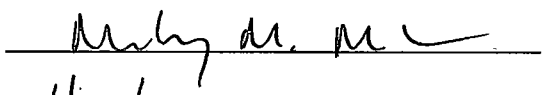
John C. Hermanson _____ 4-23-01
(Signature) Date

Approved for the College of Graduate Studies

Bruce R. McLeod _____ 4-23-01
(Signature) Date

STATEMENT OF PERMISSION TO USE

In presenting this dissertation in partial fulfillment of the requirements for a doctoral degree at Montana State University, I agree that the Library shall make it available to borrowers under the rules of the Library. I further agree that copying of this dissertation is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Requests for extensive copying or reproduction of this dissertation should be referred to Bell & Howell Information and Learning, 300 North Zeeb Road, Ann Arbor, Michigan 48106, to whom I have granted "the exclusive right to reproduce and distribute my dissertation in and from microform along with the non-exclusive right to reproduce and distribute my abstract in any format in whole or part."

Signature 

Date 4/23/01

ACKNOWLEDGEMENTS

I would like to thank Dr. Stephen Hill for providing me with the opportunity to work on such a rich and exciting project. I would also like to express my deepest appreciation to Norman Williams for his patience and guidance in the machine shop, and Margaret Jarrett for her overwhelming support during the last six years.

Finally, I am truly indebted to my friends and family, who have provided tremendous support during my tenure at MSU. In particular, I would like to thank my wife, Cynthia Kiehn, for her monumental patience while I completed my degree.

TABLE OF CONTENTS

LIST OF TABLES

Table

LIST OF FIGURES

Figure

ABSTRACT

This dissertation explores the superconducting, mixed state phase diagram of the layered organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. In particular, the melting of the quasi-two-dimensional (Q2D) vortex lattice is investigated throughout a wide range of the available field and temperature parameter space. At moderate fields (0.01 – 2 tesla) and temperatures (1.5 – 10 kelvin), a cavity perturbation technique is used to study the Josephson plasma resonance. By investigating this phenomenon over a wide frequency, field, and temperature range, one can determine a line in the phase diagram that corresponds to either a flux lattice melting or depinning transition. For high fields (2 – 20 tesla) and low temperatures (0.025 – 0.300 kelvin) cantilever beam torque magnetometry is used to determine the melting of the Q2D flux lattice. In this regime, it is shown that this transition is due to quantum fluctuations in the positions of the vortices. From the results of these two experiments, one can piece together the mixed state phase diagram. Upon doing so, it is seen that the Q2D flux solid and vortex liquid states dominate the majority of the phase diagram.

INTRODUCTION

Low dimensional conductors

Anisotropy, or low dimensionality, plays a fundamental role in many areas of contemporary condensed matter physics, both pure and applied. For example, much of the technology that has revolutionized the microelectronics industry in recent years has resulted from the development of low dimensional semiconductor devices. More recently, research into bulk layered materials such as the transition metal oxides [1], organic conductors and superconductors [2], semiconductor superlattices [3], magnetic nanostructure [4], etc., has resulted in the discovery of a range of new physical phenomena, e.g., high temperature superconductivity [5], colossal magnetoresistance [6], and a novel form of the quantum Hall effect [7]. Many of these discoveries challenge basic understanding of condensed matter physics, while, at the same time, may hold the key to further technologies. This thesis will focus on one of the above-mentioned classes of materials; an organic superconductor based on the bis-ethylenedithio-tetrathiafulvalene cation, [abbreviated as BEDT-TTF, or more simply ET (see figure 1)], which has a quasi-two-dimensional (Q2D) character due to its layered crystal structure, and will be discussed in detail below.

BEDT-TTF based conductors and superconductors. In the same way that atoms may be brought together to form conventional solids, large organic molecules may also be used as the basis for building stable crystals, with the added benefit that the crystal properties can be changed by chemically altering the basis molecule [2]. This added

degree of freedom allows chemists to synthesize materials with a wide variety of properties, which depend solely on the underlying chemical structure of the constituent organic molecules. In particular the organic charge transfer salts (CTS), so called due to the partial transfer of electrons between the constituent molecules, have provided a fertile source of novel physical phenomenon, including spin and charge density wave formation, superconductivity, antiferromagnetic behavior, etc [2]. Of the CTS, perhaps the most widely studied family is that based on the BEDT-TTF molecule. The first organic superconductor based on this ET cation was $(ET)_2(ReO_4)_2$, which was synthesized in 1983, and had the modest T_c of 2.0 K [8]. Shortly after that, many more organic conductors and superconductors followed with the same stoichiometry, $(ET)_2X$ [2]. Note that although there exist other stable stoichiometries, the 2:1 variety is the most widely studied, and will be the only case considered in this thesis.

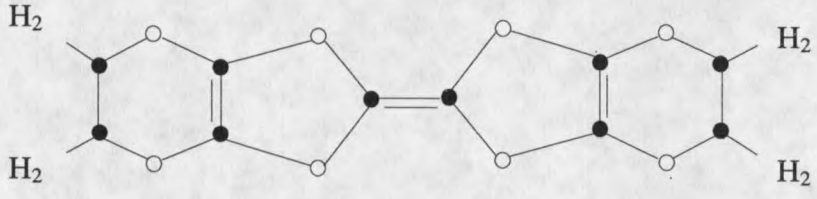
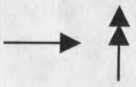


Figure 1. The nominally flat ET molecule. The carbons (•) and sulfurs (o) are strongly σ-bonded within the plane of the molecule, while the π-orbitals on the sulfurs lie perpendicular to the plane of the molecule, and are responsible for the conduction properties of ET based CTS.

For this particular subset of CTS, there is both an ionic and covalent nature to the bonding between the ET cation and the inorganic anion, and between the individual ET cations. Hence, each pair of ET molecules jointly donates a single electron to the anion X, resulting in the following basis for building stable crystal structures [2]:

$(ET)_2 + X \rightarrow (ET)_2^+ e^- + X \rightarrow (ET)_2^+X^-$ 

This is quite similar to the ionic bonding found in traditional inorganic salts such as NaCl. However, as mentioned above, there is also a considerable covalent character to the inter-molecular bonding, which will be shown to give rise to the conduction by these CTS.

Within each ET molecule, the intra-molecular bonds between the atomic species originate from the overlap of hybridized s and p atomic orbitals of the carbon and sulfur atoms within the rings, thereby producing strong σ-bonds [2]. This is quite analogous to the σ-bonding found in the much simpler organic compound, benzene. In this case, the 2s and 2p atomic orbitals hybridize within the plane of the molecule, and overlap to form the σ-bonds between the carbons. This leaves one remaining 2p atomic orbital on each carbon, to form the π-orbitals, which lie normal to the plane of the ring (see figure 2). Whereas the σ-electrons are tightly bound between adjacent carbons in the benzene molecule, the π-electrons are much more loosely bound, and will tend to delocalize around the entire ring [9].

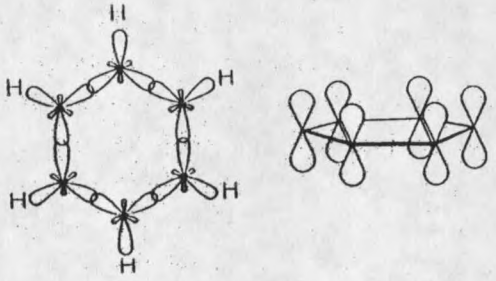


Figure 2. The planar benzene ring. The 2s and 2p atomic orbitals for each carbon hybridize, and then overlap with those on adjacent atoms to form strong σ-bonds (left). The remaining p orbitals lie normal to the plane of the molecule (right) and form the π-orbitals, with loosely bound electrons.

Like benzene, each ET molecule also exhibits π-bonding due to the overlap of the atomic p orbitals of the sulfurs within each ring. However, in the solid state, the π-electrons can delocalize over the entire crystal, rather than solely within a single molecule, so long as there are significant π-orbital overlap. Hence, it is the overlap of the π orbitals within the ET based CTS which are responsible for the bandstructure, i.e., electronic conduction [2].

To understand the band structure of these materials, one must imagine building a crystal one molecule at a time. Thus, if there are N total molecules in the system, then before the solid is assembled, the system will have a series of N-fold degenerate energy levels. However, as the isolated molecules are brought together, that degeneracy is lifted, due to the overlap of π-orbitals between each ET molecule and its neighbors. The energy levels broaden from sharp N-fold degenerate levels into non-degenerate energy bands. The widths of these energy bands will depend explicitly on the amount of inter-molecular π-orbital overlap. This is seen in figure 3 for the simplified case of a hydrogenic atom. On the left side of the figure, the N-fold degenerate atomic energy levels are shown, which broaden into bands as the atoms are brought closer together in the formation of a solid (right side of the figure) [10]. Due to the directional nature of the π orbitals on the ET molecules, i.e., the lobes of the orbitals lie perpendicular to the plane of the ET molecule, the orbital overlap is expected to be highly anisotropic. Consequently, the way in which the molecules pack together to form a crystal structure, will essentially determine the dimensionality of the conductor.