Layered Molecular Conductors with Organic Counterions

Molecular Materials Group — Materials Science Division — Argonne National Laboratory

Urs Geiser, Aravinda M. Kini, John A. Schlueter, Hau H. Wang

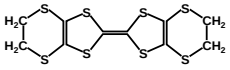
Introduction

Superconductivity with a transition temperature, T_c = 5 K was found by our group in the all-organic electron donor radical salt β"-$(ET)_2SF_5CH_2CF_2SO_3$. We have explored both the chemistry and the physics (in collaboration with others) of this system, in order to:

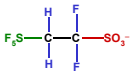
(a) understand the nature of superconductivity, esp. the role of interlayer coupling interactions

(b) understand the nature of the normal state

(c) study related compounds made by substitutions of the anion, in order to explore the boundaries of the superconducting chemical phase space and the electronic properties of the salts on the other side of these boundaries.



ET or bis(ethylenedithio)tetrathiafulvalene. This organic electron donor molecule has yielded the large majority of all organic superconductors.



$SF_5CH_2CF_2SO_3^-$ anion. Possible chemical modifications include: (a) replace SF_5 head group; (b) change carbon chain length; (c) H/F substitution pattern on backbone; (d) replace anionic tail group.

The organic conductor salts contain alternating layers of donor radical cations and charge-compensating anions and are therefore extremely anisotropic. The highlights of this poster all illustrate various aspects of the importance of interlayer interactions.

The Origin of the Universal Inverse Deuterium Isotope Effect in Organic Superconductors

In collaboration with the groups of Michael Lang (Max Planck Institute for Chemical Physics of Solids, Dresden, Germany and University of Frankfurt a. M., Germany) and Gary L. Gard (Portland State University).

One of the longstanding questions in organic superconductivity related to the origin of the "inverse" isotope effect has been resolved. Continuation of our isotope effect studies has recently revealed that the "inverse" isotope effect, i.e., increase in T_c upon substitution by heavier isotope, is present in three different superconductors with different molecular packing motifs and different types of anions.

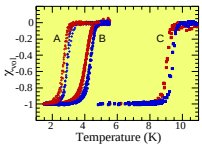
AC susceptibility for the protonated (red) and deuterated (blue) forms of

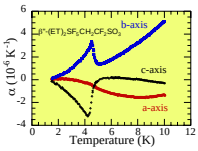
(A) κ$_L$-$(ET)_2Ag(CF_3)_4(C_2H_2Br_2Cl)$, T_c = 2.90 K

(B) β"-$(ET)_2SF_5CH_2CF_2SO_3$, T_c = 4.34 K

(C) κ-$(ET)_2Cu(SCN)_2$, T_c = 9.20 K

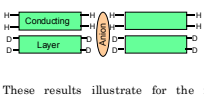
The magnitude of the isotope shift is essentially identical in all three superconductors, +0.26 ± 0.06 K.





High-resolution measurements of the coefficients of thermal expansion in β"-$(ET)_2SF_5CH_2CF_2SO_3$ (see figure on the left) and κ-$(ET)_2Cu(SCN)_2$ have revealed large negative uniaxial pressure derivatives perpendicular to the conducting planes that are of nearly the same magnitude, $(\partial T_c/\partial p)_\perp$ = –5.9 ± 0.25 and –6.2 ± 0.25 K/kbar respectively.

These two results, when taken together, strongly suggest that the "inverse" deuterium isotope effect in layered ET-based organic superconductors is caused by negative "internal lattice pressure." This negative pressure is due to the shorter C–D bonds that are oriented nearly perpendicular to the conducting planes (C–D bonds have smaller zero point displacements compared to C–H bonds).



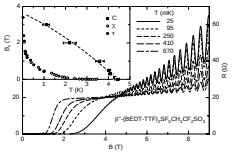
Schematic representation of two conducting layers formed by ET molecules (green) with hydrogen or deuterium atoms pointing at the anion layer or approximately perpendicular to the layers.

These results illustrate for the first time that pressure (mechanical or chemical) applied perpendicular to the conducting sheets sharply decreases the superconducting transition temperature, whereas, in-plane pressure increases T_c. Thus, higher T_c's are expected in this class of materials if the interlayer distance is increased and the distance between ET stacks within a conducting sheet is decreased.

Shubnikov-de Haas Oscillations in the Superconducting State of β"-$(ET)_2SF_5CH_2CF_2SO_3$

In collaboration with the groups of Jochen Wosnitza (University of Karlsruhe., Germany) and Gary L. Gard (Portland State University).

Shubnikov-de Haas (SdH) oscillations were observed in β"-$(ET)_2SF_5CH_2CF_2SO_3$ at or just below the upper critical field (B_{c2}) of 3.6 T. The upper critical field was determined from heat capacity measurements, while the irreversibility line was observed both in the magnetic susceptibility and from torque measurements (inset).



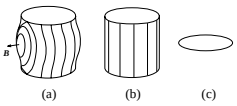
Two factors contribute to the observation of magnetoresistance oscillations at such low fields:

1. The all-organic salts are free of magnetic impurities. In contrast, it is very difficult to see any oscillations at all in κ-$(ET)_2Cu[N(CN)_2]Br$ which is known to contain paramagnetic Cu^{2+} impurities at the parts-per-million level.
2. The interlayer coupling in the all-organic superconductor is much weaker and incoherent (see next topic), in contrast to most other molecular superconductors. Therefore, a large reversible region exists below B_{c2} where the vortices are free to move, and a finite resistivity exists. The corrugation of the Fermi surface is essentially absent, hence all electrons contribute to the SdH effect even though their density is low (~ 10^{21} cm^{-3}).

Absence of Magnetoresistance Coherence Peak in an All-Organic Superconductor

In collaboration with the groups of John Singleton (Oxford University) and Jochen Wosnitza (University of Karlsruhe, Germany).

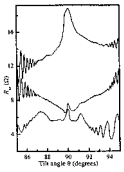
Most organic superconductors are characterized by a Fermi surface (FS) that contains approximately cylindrical segments. Interlayer interactions are small but not negligible. The question of coherence in the interlayer transport arises. Three cases are possible:



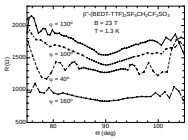
(a) Quasi two-dimensional FS with three-dimensional contributions to the band structure. Magnetoresistance enhancement due to cyclotron orbits around the "bulge" (shown exaggerated) when the magnetic field is parallel to the conducting plane. Coherent interlayer transport.

(b) Negligible corrugation of the FS but still coherent transport.

(c) No coherence in the interlayer direction; strictly two-dimensional system.



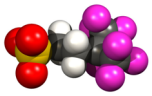
The molecular superconductors β-$(ET)_2I_3$, κ-$(ET)_2Cu(NCS)_2$, and κ-$(ET)_2Cu[N(CN)_2]Br$ all showed an enhancement of the magnetoresistance when the angle between the magnetic field (larger than the upper critical field, therefore in the normal state) was perpendicular to the layer normal. The interlayer transport is therefore coherent. This is shown for κ-$(ET)_2Cu(NCS)_2$ in the figure on the left for three different in-plane azimuthal angles.



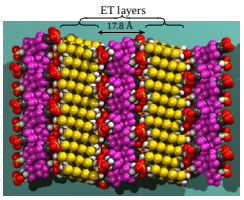
In marked contrast, in the all-organic superconductor β"-$(ET)_2SF_5CH_2CF_2SO_3$ there is no enhancement. Thus, three-dimensional interactions do not contribute to the Fermi surface. The all-organic superconductor is therefore much more two-dimensional than the other salts studied.

Extreme Conducting Layer Separation in an Electron Donor Radical Salt with Highly Fluorinated Organic Anion — Fluorophilic Effect

Organic sulfonate anions similar to that found in the all-organic superconductor β"-$(ET)_2SF_5CH_2CF_2SO_3$ offer many avenues for chemical substitution in order to fine-tune the crystal structure and therefore the physical properties. We have thus succeeded in the synthesis of the ET salt with the largest separation of the ET conducting layers to date. The thickness of the interlaced anion layer is 17.8 Å in $(ET)_3[SO_3C_2H_4CF(CF_3)_2]_4(H_2O_2)_2$.



Above: $SO_3C_2H_4CF(CF_3)_2^-$ anion. Carbon atoms are gray, sulfur yellow, oxygen red, fluorine purple, and hydrogen white. Right: Crystal structure of the ET salt of the same anion.



The unusual self-assembly of the anion into bilayers is an expression of the *fluorophilic* effect: organofluoro substituents are incompatible both with polar, hydrophilic as well as with hydrocarbon-like, hydrophobic functionalities. Therefore, areas of high fluorine substitution tend to aggregate together, an effect that is exploited technically, e.g. in fluorocarbon (Teflon®) protective coatings.

Summary

The topics presented here represent different aspects of interlayer interactions:

⇒ The isotope effect study relates a geometrical (bond length) effect to the dependence of T_c on the anisotropic pressure perpendicular to the conducting layers.

⇒ The observation of SdH oscillations belong the upper critical field is made possible by the unusual vortex state that is principally unique in two-dimensional materials.

⇒ The magnetoresistance study probes interlayer electrical transport phenomena, especially the question of coherence.

⇒ The fluorophilic effect exemplifies an avenue to build, by chemical means, organic radical cation salts with extremely large layer separations in order to increase the electronic anisotropy.

Future Plans

- The synthesis effort will be expanded to include magnetic counterions with the goal of hybrid conducting/ordered magnetic systems.
- The fluorophilic effect will be utilized to synthesize more highly conducting donor radical salts with bilayer anions.
- The recently discovered 40 K spin-Peierls system β'-$(ET)_2SF_5CF_2SO_3$ will be examined in order to understand why a structurally two-dimensional material can exhibit this phenomenon characteristic of a one-dimensional system.
- The donor radical salts with organic counterions will be fabricated into field-effect transistors in order to induce higher conductivity and even superconductivity by charge injection (with John Carlisle, FWP 57504, and Ken Gray, FWP 58916).
- The superconductor β"-$(ET)_2SF_5CH_2CF_2SO_3$ has recently been found to undergo an unusual pressure-induced transition to an insulating ground state. The nature of this transition will be examined.
- Thin films of organic conductors will be prepared by means of the self-assembly technique on top of chemically modified surfaces.

This work was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contract W-31-109-ENG-38.

FWP 58510