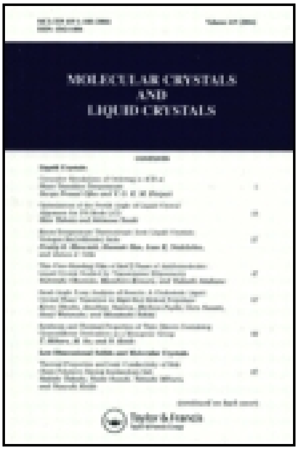

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The search for new superconductors at argonne national laboratory

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THE SEARCH FOR NEW SUPERCONDUCTORS AT ARGONNE NATIONAL LABORATORY

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The organic superconductors program at Argonne National Laboratory was started by Jack M. Williams in 1981. Initial studies centered around structural effects in the TMTSF salts. Since 1984, the major emphasis has been on salts of the electron donor bis(ethylenedithio)tetrathiafulvalene (ET). Important milestones include the discovery of a number of new superconductors, among them: β*-(ET)*$_2$*IBr*$_2$ *(*$T_c = 2.8\,K$*) and* β*-(ET)*$_2$*AuI*$_2$ *(*$T_c = 4{-}5\,K$*). These salts led to the first structure-properties relationship in ET salts.* κ*-(ET)*$_2$*Cu[N(CN)*$_2$*]Br (*$T_c = 11.8\,K$*, ambient pressure) and* κ*-(ET)*$_2$*Cu[N(CN)*$_2$*]Cl (*$T_c = 12.5\,K$ *at 0.3 kbar pressure) are still the cation radical superconductors with the highest known transition temperatures. The families of* κ_L*- and* κ_H*-(ET)*$_2$*[M(CF*$_3$*)*$_4$*](solvent) salts (*$T_c = 2{-}11\,K$*) yielded at least 25 new closely related organic superconductors with M = Cu, Ag, Au, and solvent = 1,1,2-trihaloethane.* β''*-(ET)*$_2$*SF*$_5$*CH*$_2$*CF*$_2$*SO*$_3$ *(*$T_c = 5\,K$*) was the first superconductor where both the radical cation and the charge balancing anion were organic. Recent results in the synthesis and characterization of ET salts with anions similar to* $SF_5CH_2CF_2SO_3^-$ *are presented.*

Keywords: organic superconductors; bis(ethylenedithio)tetrathiafulvalene; history

INTRODUCTION

In 1979, when superconductivity was discovered in $(TMTSF)_2PF_6$ (reported in the literature in 1980) [1], the Argonne group, in the Chemistry Division, headed by Jack M. Williams (JMW) was a totally different

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"beast" than it is today. It had strong components in structural chemistry, primarily in single crystal X-ray and neutron diffraction. The Argonne research reactor CP-5, where JMW had a beam line had recently been shut down, but the spallation neutron source IPNS had come on-line in its place, and the group was able to retain a presence there by placing Arthur J. Schultz as an instrument scientist at the single crystal diffraction facility. Centered around the structural chemistry were scientific programs in hydrogen bonding, catalyst structure and function, and (most important for the future direction of the group) electrically conducting platinum chain materials.

It was due to the latter that JMW attended the International Conference on Synthetic Metals in 1979 in Helsingør, Denmark, and heard about the breakthrough discovery of superconductivity in organic charge transfer salts. After his return, he was able to obtain support to build up a program in organic conductors that eventually became the sole focus of his group.

THE PEOPLE

The enormous success of the Argonne group in discovering a large number of organic superconductors was in a large part due to the teamwork of a core of staff scientists supplemented with a steady stream of postdoctoral associates and undergraduate student interns. The scientific staff in the group during that period were:

Jack M. Williams, senior scientist and group leader until his retirement for health reasons in 1997 was the founder of the program. The other members of the group were hired at his instigation.

Arthur J. Schultz. By 1980, AJS was already promoted to scientific staff. His primary duty continues today as instrument scientist of the single crystal diffractometer at IPNS. He transferred out of the group into the IPNS organization in 1993.

Mark A. Beno was a postdoctoral fellow in 1980. In 1982, he was promoted to scientific staff. He worked in the group principally as a single crystal X-ray diffraction specialist and built among others a diffractometer capable of reaching sample temperatures as low as 10 K.

K. Douglas Carlson, a senior physical chemist, joined the group as a result of a major reorganization in 1983. He built up the necessary capabilities within the group to characterize electrical and magnetic properties of the many newly discovered materials. He retired in 1995. The same reorganization brought the group programmatically into the Materials Science Division at Argonne, as well as within the Department of Energy structure, although an affiliation with the Chemistry Division remained until 2000.

H. Hau Wang joined the group in 1983 as a postdoctoral appointee (staff scientist, 1985) to strengthen the synthesis and crystal growth expertise necessary for the realization of novel materials. He is still a member of the program.

Aravinda M. Kini, a staff scientist hired in 1986, further strengthened the synthetic capabilities of the program, especially in the area of organic donor design. He is still a member of the program.

Urs Geiser (postdoc 1985, staff scientist 1988) is a structural and physical chemist. He took over primary responsibility for the X-ray diffraction work after Mark Beno's transfer and took on some of K. D. Carlson's duties after the latter's retirement. After JMW's departure, he served as Acting Group Leader for almost three years.

John A. Schlueter first joined the group as a student intern during the summers of 1986 and 1987. After he finished graduate school, he rejoined the program as a postdoc in 1992, and in 1995 he was promoted to staff scientists. He is active in anion synthesis, crystal growth, as well as magnetic properties measurements.

MILESTONES

During the first few years after the discovery [1,2] of superconductivity in $(TMTSF)_2PF_6$, the Argonne group studied the detailed crystal structure of a large number of these salts in order to establish a relationship between the superconducting properties and structural parameters, as well as the correlations between structural variables, e.g., unit cell volume vs. anion volume (in order to arrive at an effective donor volume) [3]. The effect of crystallographic anion disorder and its influence on the cooling rate dependence of superconducting properties was thoroughly discussed [4]. During this period, highly conducting salts of BEDT-TTF or ET were discovered [5], and soon the emphasis of the work at Argonne shifted toward salts of the latter donor molecule.

β-$(ET)_2X$ ($X^- = I_3^-$, IBr_2^-, AuI_2^-)

The discovery of superconductivity at ambient pressure in what we now know as the low-T_c (1.4 K) phase of β-$(ET)_2I_3$[6] stimulated a large worldwide effort in finding analogs with possibly higher transition temperatures. Our program was the first to succeed with the ET salt of the related anion IBr_2^- with T_c of 2.8 K [7]. From the comparison of the two salts, it was erroneously concluded that smaller anions would therefore lead to higher superconducting transition temperatures. Two further discoveries however led to the reversal of this view: (1) The discovery of superconductivity near 5 K in β-$(ET)_2AuI_2$ (AuI_2^- is intermediate in size between IBr_2^- and I_3^-), again by the Argonne group [8], and the realization of the metastable high-T_c (8 K) or β_H-phase of β-$(ET)_2I_3$ through the application of pressure [9,10]. The latter is more comparable to the other salts because it lacks the presence of a modulated low temperature crystal structure, which leads to random potentials and a suppression of the superconducting transition temperature. The modulated structure of β-$(ET)_2I_3$ was studied in detail by members of the Argonne group [11], as was the structure of β_H-$(ET)_2I_3$ [12].

κ-$(ET)_2Cu[N(CN)_2]X$ (X = Br, Cl)

With the realization that polymeric complexes based on the cuprous ion could serve as suitable anions for superconducting ET salts such as κ-$(ET)_2Cu(NCS)_2$ [13], we explored a variety of pseudohalide ligands to replace thiocyanate. One of these was dicyanamide, $N(CN)_2^-$. However, the intermediate that was isolated in order to carry out the electrocrystallization process to prepare hypothetical $(ET)_2Cu[N(CN)_2]_2$ actually contained the $Cu_2[N(CN)_2]_3Br^-$ anion, and the ET salt that formed was κ-$(ET)_2Cu[N(CN)_2]Br$, a superconductor with $T_c = 11.6$ K, which remains the highest transition temperature for any donor radical salt at ambient pressure [14].

We immediately set out to search for the halogen analogs of this salt, and κ-$(ET)_2Cu[N(CN)_2]Cl$ was found to be isostructural, but required a slight amount of pressure to induce superconductivity with a maximum transition temperature of 12.6 K [15]. At ambient pressure, the ground state is a slightly canted antiferromagnet below ca. 26 K [16,17]. Well over 200 papers have resulted from the extensive study of the physical properties of the κ-$(ET)_2Cu[N(CN)_2]X$ salts to date.

κ-$(ET)_2M(CF_3)_4(C_2H_3X_3)$ (M = Cu, Ag, Au; X = Cl, Br)

The period of the early 1990s saw a return to discrete anions. As by this time ET salts with almost all simple inorganic anions had been synthesized, we started to investigate larger, more complex anions. Through a collaboration with a group in Cologne, Germany, we were able to obtain the series of organometallic anions $Cu(CF_3)_4^-$, $Ag(CF_3)_4^-$, and $Au(CF_3)_4^-$. The ET salts of these anions form two large families of superconductors with T_cs between 2 and 11 K [18–20]. Both families incorporate co-crystallized trihaloethane solvents, which allows for the large number of members that differ in the halogen substitution pattern of the solvent molecule in addition to the identity of the anion metal center. The two families are structurally distinct and may be separated by morphology. Unfortunately, only the low-T_c κ_L family (plates) is structurally characterized, whereas no crystals of sufficient quality for an X-ray diffraction study were ever obtained from the high-T_c κ_H family (fine needle bundles). Both types are susceptible to solvent loss concomitant with conversion to a semiconducting phase. A comparison of T_c with structural parameters of the κ_L-phase revealed a dependence both on interlayer spacing (positive correlation) and intralayer spacing (negative correlation) [21].

β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$

The success with the organometallic anions led us to further explore new types of large discrete anions, and a collaboration was formed with the fluorine chemistry group of G. Gard in Portland, Oregon, who provided us with fluorinated sulfonate anions. Among the first of these was $SF_5CH_2CF_2SO_3^-$, which upon electrocrystallization with ET led to the first all-organic radical cation-based superconductor, β''-$(ET)_2SF_5CH_2CF_2SO_3$ with T_c around 5 K [22]. The complete absence of paramagnetic impurities in this salt make this one of the most ideal systems to study superconducting and normal state properties, and it was found to exhibit Shubnikov-de Haas oscillations in magnetic fields even below the upper critical field [23]!

CURRENT RESEARCH

The anion in β''-$(ET)_2SF_5CH_2CF_2SO_3$ held great promise for chemical substitutions that should lead to other superconducting salts. Four types of modifications may be made: (1) substitution of the SF_5 head group by CF_3 and other fluorinated groups; (2) replacement of the anionic group by selenonate, phosphonate etc.; (3) variation of the carbon backbone length; (4) change in the hydrogen:fluorine substitution pattern. A large portion of our effort in the last few years has been in the realization of these anion modifications, and a large number of salts have been synthesized [24–26]. However, no additional superconductors were found. Instead, most of the salts exhibited electron localization at low temperature, often by charge disproportionation, and not all adopted the β'' structural type of the superconductor. Even the incorporation and complexation of lithium electrolyte counterion by the sulfonate anion was found in one example, $(ET)_2Li(CF_3CHFSO_3)$ [26].

A reorganization in 2000 incorporated the program into the Molecular Materials Group led by Larry A. Curtiss. Besides the conductors program, the group also has experimental components in molecular magnets, diblock copolymers, mesoporous solids, and organized fluids, as well as a strong computational theory program. These various programs are expected to strengthen the interdisciplinary nature of the research and lead to new hybrid materials that combine the most interesting properties of some of the above. Furthermore, the interaction of these various research areas should lead to exciting new materials in the emerging field of nanoscience.

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