phonon scattering to "rattle in the cages." The increased scattering should produce a greatly reduced lattice thermal conductivity and thus has the possibility of greatly enhancing the figure of merit for these materials (*5*). From Slack's minimum thermal conductivity theory (*7*), it is estimated that the thermal conductivity in these skutterudite materials could be lowered by as much as a factor of 40 by filling these voids. For example, Nolas *et al.* found large reductions (by a factor of 20) in λ_L by void filling in the $IrSb_3$ system (*6*). In general, these skutterudite materials meet many of the basic criteria for a material to exhibit a high *ZT*, as pointed out by Slack: large, complex unit cell with heavy constituent atoms, high mobility carriers, and a small band gap. Sales *et al.* (*3*) present very promising results on the properties of "filled skutterudites" based on $CoSb_3$ (specifically $LaFe_3CoSb_3$ and $CeFe_3CoSb_3$), which further indicate that when fully optimized, this family of compounds may lead to much higher performance thermoelectric materials.

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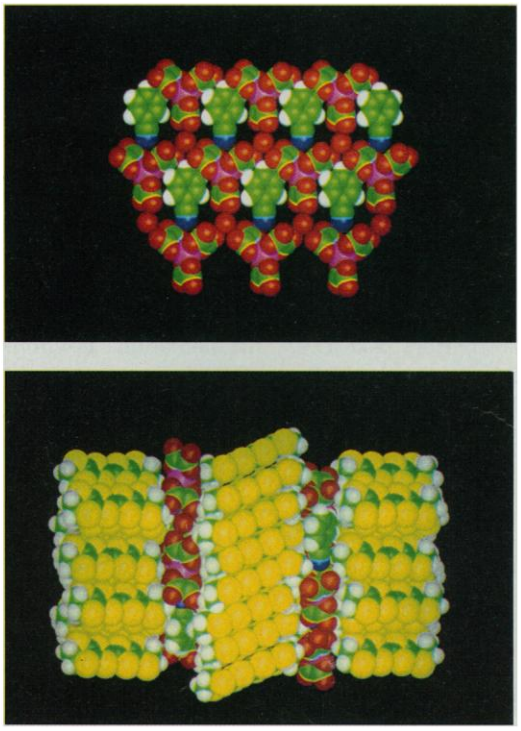
A Molecular Paramagnetic Superconductor

Patrick Cassoux

Superconductors consisting of molecular solids (as opposed to metals) present a variety of technological opportunities, and understanding how they work is essential before applications can follow. It has long been thought that the presence of magnetic ions in the molecular structure should decrease or even suppress superconductivity. Recently, however, Kurmoo *et al.* (*1*) prepared and characterized the first example of a molecular superconductor containing iron(III) magnetic anions. These results contradict our preconceived notions about the coexistence of magnetism and superconductivity and, more generally, our ideas about systems exhibiting interaction between conduction electrons and localized spins.

Most molecular superconductors are electron-transfer salts of the type $(BEDT\text{-}TTF)_2A$, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene and A is a counteranion. The anion A may be octahedral (such as $[PF_6]^-$), tetrahedral ($[ClO_4]^-$), linear ($[I_3]^-$), or polymeric ($[Cu(NCS)_2]^-$) (*2*). The highest superconducting critical temperature T_c observed to date for a molecular superconductor is 12.8 K in the κ-$(BEDT\text{-}TTF)_2(Cu[N(CN)_2]Cl$ phase (*3*). In none of these molecule-based superconducting salts is the counter anion A magnetic; that is, none of these salts contains localized anion spins.

The application of a magnetic field suppresses superconductivity (the Meissner effect), as do internal magnetic fields generated in ferromagnetic materials. This effect may be understood within the framework of the Bardeen-Cooper-Schrieffer theory (BCS) for three-dimensional systems exhibiting a spherical Fermi surface (*4*). According to BCS theory, the occurrence of singlet-state superconductivity results from the pairing of electrons having opposite spins (Cooper pairs). This pairing is mediated by lattice vibrations and can be disrupted by the close vicinity of magnetic impurities. These impurities must only be sufficiently diluted, that is, paramagnetic and thus without either short- or long-distance magnetic order. For example, a few parts per million of iron prevent molybdenum from becoming superconducting; this observation has been also made for the commonly used superconducting alloys of transition metals.



The anionic (**top**) and cationic (**bottom**) layers in the paramagnetic molecular superconductor β″-$(BEDT\text{-}TTF)_4(H_2O)[FeCC_2O_4)_3]\cdot C_6H_5CN$. [Courtesy: P. Day]

Several attempts have been made to couple interesting conducting and magnetic behaviors in a molecular compound. A first example was given by the [TTF] $[MX_4C_4(CF_3)_4]$ compounds (M = Cu, Au; X = S, Se), which exhibit low conductivities but undergo a unique, so-called spin-Peierls, second-order transition at low temperatures to a nonmagnetic state (*5*). The $[2,5\text{-}XY\text{-}DCNQI]_2Cu$ compounds (DCNQI = *N,N′*-dicyanoquinone diimine; X, Y = Me, Cl, Br) were shown to exhibit metallic properties down to low temperatures and a ferromagnetic ordering of the copper spins (*6*). In the $(perylene)_2[M(mnt)_2]$ compounds (M = transition metal; mnt = maleonitriledithiolate, $[C_4N_2S_2]^{2-}$), instabilities typical of one-dimensional conducting (Peierls instability, for the perylene chains) and magnetic [spin-Peierls instability, for the $M(mnt)_2$ chains] systems were observed (*7*).

The first examples of BEDT-TTF–based metals incorporating magnetic anions—such as FeX_4^- and CuX_4^-, with X = Cl, Br—have been reported by Day *et al.* (*8*). Although these materials did exhibit interesting conducting and magnetic properties, none of them showed superconducting behavior. Further work along this line by Kurmoo *et al.* (*1*) showed that the β-$(BEDT\text{-}TTF)_4[(H_2O)Fe(C_2O_4)_3]\cdot C_6H_5CN$ phase does more than its forerunners. This salt exhibits a sharp (width about 0.2 K) superconducting transition with a T_c of 7.0 K, which is rather high for a molecule-based system. The magnetic susceptibility above T_c is a sum of a Pauli component typical of a metal and

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a Curie-Weiss term from the very weakly antiferromagnetically coupled Fe^{3+} ions. Below T_c, the susceptibility increases with increasing field until it reaches a critical field, which is consistent with a London penetration depth. The Meissner effect is complete at 0.5 mT. The electron paramagnetic resonance spectra show one Dysonian in shape resonance due to the conduction electrons of the BEDT-TTF chains and one Lorentzian in shape resonance due to the Fe^{3+} ions. Electronic band structure calculations based on crystal data obtained at 300 K confirm a metallic behavior with both electron and hole pockets in the Fermi surface (which are, more probably, tubes resulting from the two-dimensional character of the crystal structure). In conclusion, this phase truly is the first molecule-based paramagnetic superconductor.

The paper by Kurmoo *et al.* also illustrates how small chemical modifications may result in drastic changes in the physical properties of molecular electron-transfer salts. The derived $(BEDT\text{-}TTF)_4[YFe(C_2O_4)_3]$ C_6H_5CN salts obtained by substituting Y = K or NH_4 or H_2O are semiconductors. This may be related to differences in the structures, which consist of layers of $(BEDT\text{-}TTF)_2^{2+}$ dimers separated by isolated neutral $(BEDT\text{-}TTF)^0$ molecules for the K or NH_4 derivatives, whereas in the H_2O derivative, chains of equivalent $(BEDT\text{-}TTF)^{+3/4}$ are observed (hence, the so-called β″-structure). By contrast, the underlying hexagonal network of Fe and Y is similar in the three compounds. Striking also is the observation of alternate $[Fe(C_2O_4)_3]^-$ anion layers that are exclusively composed either of Δ or Λ enantiomers, even though the three compounds were prepared from racemic $[Fe(C_2O_4)_3]_3^-$ starting salts.

If the behavior of $\beta\text{-}(BEDT\text{-}TTF)_4[(H_2O)Fe(C_2O_4)_3]{\cdot}C_6H_5CN$ is a result of BCS singlet-state superconductivity, then the Fe^{3+} ions cannot be directly immersed in the gas of electrons condensed in pairs; instead, they must be shielded from the superconducting BEDT-TTF layers. A similar situation is encountered in the two-dimensional high-T_c copper oxides, in which the presence of magnetic impurities suppresses superconductivity when located in the Cu-O planes but not when located outside of these planes. Another explanation may be found in the possible existence of triplet-state superconductivity, which has been suggested to be more appropriate for describing the behavior of molecular superconductors and less sensitive to magnetic perturbation (*9*). Be that as it may, the finding of Kurmoo *et al.* is a major breakthrough in the field and opens up brilliant prospects for the interplay of conductivity and magnetism in molecular solids.

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The Origin of Programmed Cell Death

Jean Claude Ameisen

Cells from multicellular organisms self-destruct when they are no longer needed or have become damaged. They do this by activating genetically controlled cell suicide machinery that leads to programmed cell death (PCD). To survive, all cells from multicellular animals depend on the constant repression of this suicide program by signals from other cells (*1*). It has been assumed that such an altruistic form of cell survival regulation arose with multicellularity and would have been counterselected in unicellular organisms (*1*). Recent findings indicate, however, that a similar process of socially advantageous regulation of cell survival also operates in single-celled eukaryotes.

PCD has now been described in four unicellular organisms (*2–5*) that emerged between 2 and 1 billion years ago and belong to three diverging branches of the eukaryote phylogenic tree (see the figure): the kinetoplastid parasites *Trypanosoma cruzi* (*2*) and *Trypanosoma brucei rhodensiense* (*3*), among the first mitochondrial eukaryotes; the free-living slime mold *Dictyostelium discoideum* (*4*); and the free-living ciliate *Tetrahymena thermophila* (*5*). Unicellular eukaryote PCD is similar (*4*)—or identical (*2*, *3*)—to apoptosis, the usual PCD phenotype in cells from multicellular animals (*1*). Its features include cytoplasmic blebbing and vacuolization, chromatin condensation, and DNA fragmentation. Environmental stress (such as starving) and extracellular signals that activate the cyclic AMP pathway (which induce differentiation to a reversible G_0/G_1-arrested stage) also induce PCD in cells that remain undifferentiated and cycling (*2*, *4*). In low-density cultures of dividing protists, PCD is induced "by default" if cell differentiation is not triggered, unless certain environmental conditions are provided (*2*, *5*). Finally, in the kinetoplastid parasites, PCD is also regulated by signals from their multicellular host (*2*, *3*). So, like multicellular organisms, survival of unicellular eukaryotes depends on the prevention of self-destruction by extracellular signals.

Why has evolution favored such a system of cell destruction? PCD allows constant selection for the fittest cell in the colony, optimal adaptation of cell numbers to the environment, and tight regulation of the cell cycle and cell differentiation. PCD may be particularly useful when cells are interacting: in the trypanosomes, PCD may regulate the communication between unicellular and multicellular organisms that allow the establishment of a stable host-parasite relation (*2*, *3*); and in the slime mold, PCD allows the induction of dead stalk cells that participate in the formation of a multicellular aggregated body (*4*).

How and when did unicellular organisms select for genes allowing cell suicide? Primitive forms of PCD occur in prokaryotes when plasmid or viral genomes compete with bacterial genomes in a bacterial colony; when bacteria from different species compete; and upon terminal differentiation of *Myxobacteria* and *Streptomyces*, which allows the transient formation of multicellular aggregated bodies (*6*). These findings suggest a multistep scenario for the emergence of death genes during evolution: in prokaryotes, (i) selection for killer genes encoding toxins used for offense in evolutionary arms races between different species, and concomitant selection for genes encoding toxin antidotes for defensive purposes; and (ii) selection for the induction of such genes in adverse environmental conditions to allow control of death and survival in cells sharing the same genome, providing a selective advantage to the

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