Recent Developments in Organic Superconductors

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Abstract. Superconductivity of radical ion salts is now well established in two families of organic conductors: the quasi-one-dimensional family to which the prototype material $(TMTSF)_2PF_6$ belongs with T_c in the one Kelvin range and the two-dimensional series with T_c up to 10 K which is illustrated by salts such as $(BEDT\text{-}TTF)_2X$ i.e $(ET)_2X$ with X= I_3, AuI_2, $Cu(NSC)_2$, etc...We first recall the instabilities which are inherent to the $(TMTTF\text{-}TMTSF)_2X$ series giving as examples the behaviour under pressure of the newly synthesized mixed sulfur-selenium compound $(TMDTDSF)_2PF_6$ and the discovery of a hidden spin density wave phase in $(TMTSF)_2ReO_4$. Secondly, we present recent experimental results about the quantization of the Hall constant in the field-induced semimetallic states of $(TMTSF)_2PF_6$ under pressure and the observation of giant magnetoresistance oscillations in the high T_c phase of β-$(BEDT\text{-}TTF)_2I_3$ illustrating the two dimensional character of the latter superconductor.

I-Instabilities in the $(TMTSF)_2X$ series

Superconductivity has always been a strong motivation for the research in organic conductors since the original suggestion by Little [1] that organic matter could provide critical temperatures near ambient conditions. This driving force has proved to be justified since superconductivity was indeed discovered in the 1K range in 1980 [2] and significant improvements have been achieved in other materials discovered more recently [3][4]. However, the nature of othe superconducting pairing in organic materials remains (as it is for high T_c's superconductors) an open question: phonon or non-phonon mediated, singlet versus triplet pairing, etc..). It becomes clear now that a better understanding of the context in which the superconducting instability sets in is a major step towards understanding organic superconductivity.

Superconductivity is only one among the various instabilities which are observed at low temperature in the isostructural series to which $(TMTSF)_2PF_6$ belongs. As shown in figure (1) the electronic properties of the sulfur or selenium series are illustrated by a generalized phase diagram. The all-sulfur compound $(TMTTF)_2PF_6$ exhibits a marked charge localization below $T_\rho \approx 200K$ which is attributed to strong on-site Coulomb repulsions [5] (1-D quantum antiferromagnet) and the onset of a 3-D spin singlet state (spin-Peierls) accompanied by a lattice distortion below 19 K[6]. However, the Br salt of the same sulfur molecule exhibits a weaker charge localization below 100 K or so and the onset of a spin modulated state below 15-19K without any visible lattice distortion[7]. Quite a different behaviour is observed instead with the all-selenium compound $(TMTSF)_2ClO_4$ as no charge localization is visible above the superconducting transition at 1.2 K under ambient pressure.

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The generalized phase diagram reveals two competitions between ground states: SP versus SDW on the one hand and SDW versus superconductivity on the other.

The charge localization and the SP-SDW competition are governed by the amplitude of the Ummklapp scattering term g3 which decreases under pressure

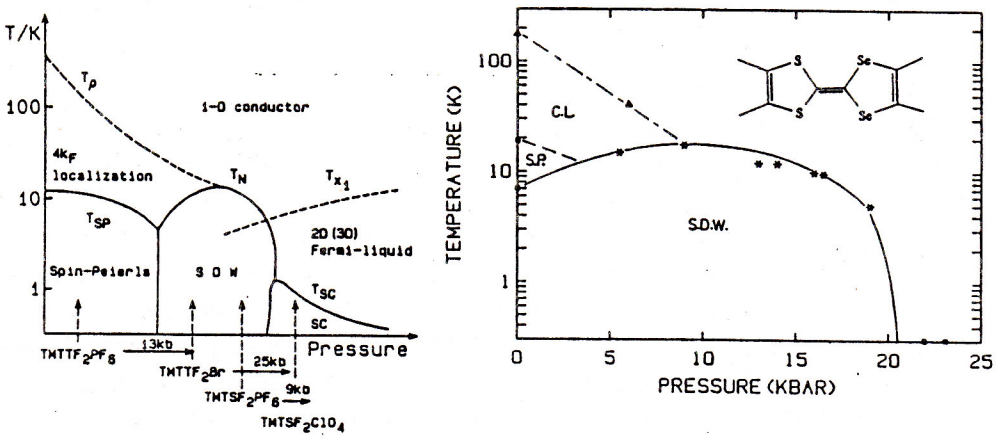

Fig.1: Generalized phase diagram of $(TMTCF)_2X$ conductors (left) and phase diagram of $(TMDTDSF)_2PF_6$ showing the reentrance of SDW below the spin-Peierls state at 7 K and the stabilization of a conducting ground state above 20 kbar (without superconductivity down to 0.4K).

and also when moving from PF_6 to Br compounds. The SDW-SC competition is very likely governed by the interplay between the SDW phase transition temperature of the Q-1-D conductor and the small energy ($\approx t^2/t//$) which characterizes the deviation of the Q-1-D Fermi surface from perfect nesting[8]. A recently synthesized S-Se hybrid molecule TMDTDSF has enabled a more thorough study of the SP-SDW competition[9]. As shown on the phase diagram of $(TMDTDSF)_2PF_6$, figure 1, a spin-Peierls ordering is detected at 19 K by its signature in the behaviour of the ESR spin susceptibility. However, the nature of the ground state which is stabilized at 7 K is clearly magnetic according to a divergence of the nuclear spin relaxation rate and the observation of antiferromagnetic resonance modes instead of a Zeeman resonance below 7K . The conducting ground state becomes stable at low temperature above 20Kbar but no superconductivity has been detected so far down to 0.4 K. At present we can think of two possible interpretations for the absence of superconductivity: the pair-breaking effect of the disorder introduced by the non-symetric organic molecule or the weakness of the interchain coupling.

The intrinsic existence of the SDW-SC competition in the TMTSF series is also revealed by a recent investigation of the phase diagram of the organic superconductor $(TMTSF)_2ReO_4$. This latter system undergoes a superconducting transition at ($\approx$10 bar) which is necessary to stabilize the ordering of the non centrosymetric ReO_4 anions with the wave vector (0, 1/2, 1/2). Below the critical pressure the stable (1/2, 1/2, 1/2) ordering doubles the lattice periodicity along the chain direction and opens a gap at the Fermi level.

The occurence of this anion-ordered semiconducting state prevents us from studying the genuine instability of the Q-1-D organic

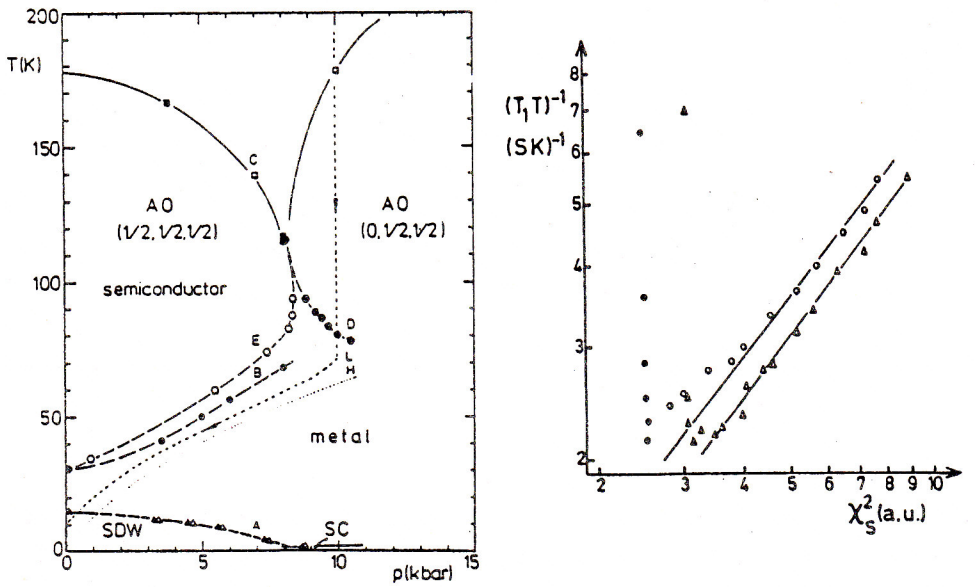

Fig.2: Observation of a SDW phase in $(TMTSF)_2ReO_4$ competing with superconductivity when a particular cooling procedure under pressure is followed (dotted line with arrows). Below 8 Kbar the anions can be frozen at low temperature in the (0, 1/2, 1/2) configuration allowing the conducting state to be stable down to the SDW or SC temperature (left). Temperature dependence of $(T_1T)^{-1}$ from ^{77}Se data plotted versus χ^2_s for $(TMTSF)_2PF_6$ (circles) and $(TMTSF)_2ClO_4$ (triangles). The departure from the straight line marks the onset of $2k_F$ low temperature spin fluctuations respectively at 100 and 30 K in PF_6 and ClO_4 salts.

stacks at low temperature. However, following a proper cooling procedure under pressure, the (0, 1/2, 1/2) configuration of the anions can be preserved at low temperature even under ambient pressure[10]. Thus, an other insulating state is revealed , figure 2, below 15 K. It is assumed that this new insulating state is analogous to the SDW phase which is stabilized in $(TMTSF)_2PF_6$ below the critical pressure.

In conclusion, the study of the $(TMTSF)_2PF_6$ and $(TMTSF)_2ReO_4$ phase diagrams have shown that the competition between antiferromagnetism and superconductivity is a firmly established character of Q-1-D superconductors irrespective of the anion symetry. The stabilization of superconductivity at a temperature higher than the 1 to 2 K range seems to be forbidden in Q-1-D conductors such as $(TMTSF)_2X$ by the intrinsic competition with

magnetic ordering. However, the border line between SDW and SC phases represents the optimum situation for superconductivity at variance with high T_c cuprate materials.

An other fact of this competition is revealed by the contribution of the low frequency antiferromagnetic fluctuations to the nuclear spin-lattice relaxation as shown in figure (2).

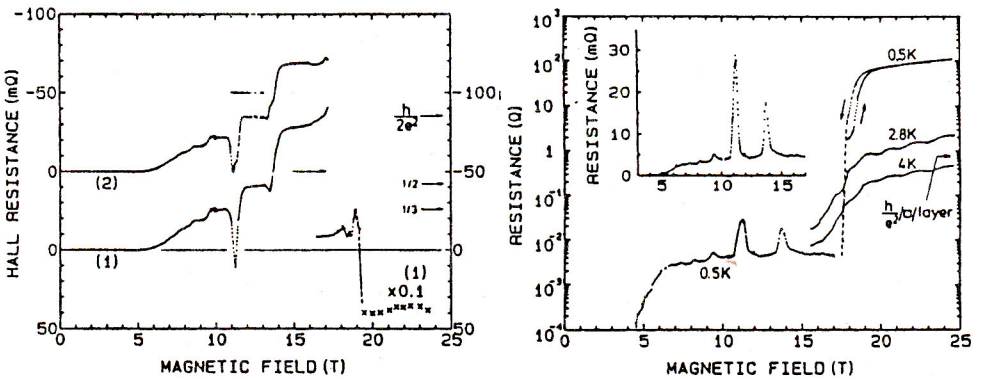

Fig.3: Hall resistance versus magnetic field along the c*axis for two $(TMTSF)_2PF_6$ samples (P ≈9 kbar, T = 0.5 K). The quantized values $h/2ne^2$=12.9/n kΩ per molecular layer are marked on the right for sample #1. The n = 0 phase is reached above 18 T (left). Magnetoresistance of the same sample up to 25T (linear scale in the inset).

As far as $(TMTSF)_2ClO_4$ is concerned the temperature dependence of $(T_1T)^{-1}$ scales with χ^2_S in the domain where uniform (q = 0) spin fluctuations are responsible for the temperature dependence of the spin susceptibility (T>30K)[11]. Below 30 K, $2k_F$ spin correlations contribute predominantly to the relaxation rate which then becomes nearly temperature independant down to the dimensionality cross-over at ≈ 8 K where a renormalized Fermi liquid description is recovered. As shown in figure 2, the effect of $2k_F$ spin correlations is even more pronounced in case of $(TMTSF)_2PF_6$ (below 100 K) at ambient pressure in agreement with the stronger tendency of that compound towards antiferromagnetism.

In conclusion, the proximity between magnetism and superconductivity is a remarkable feature of $(TMTSF)_2X$ like materials. In addition, NMR studies indicate that the long range superconductivity order develops in a superconductivity background of strong antiferromagnetic fluctuations. Some theoretical approaches have used these experimental facts to propose a pairing mechanism in $(TMTSF)_2X$ based on the interchain exchange of antiferromagnetic spin fluctuations[12].

II - Fermiology in organic conductors.

The open and quasi planar nature of the Fermi surface of $(TMTSF)_2X$ materials is illustrated

by the influence of the magnetic field on the stability of the conducting ground state. Figure 3 reports recent data of Hall effect and magnetoresistance obtained in $(TMTSF)_2PF_6$ under pressure (when the material undergoes a superconducting transition at 1.2 K[13]. The

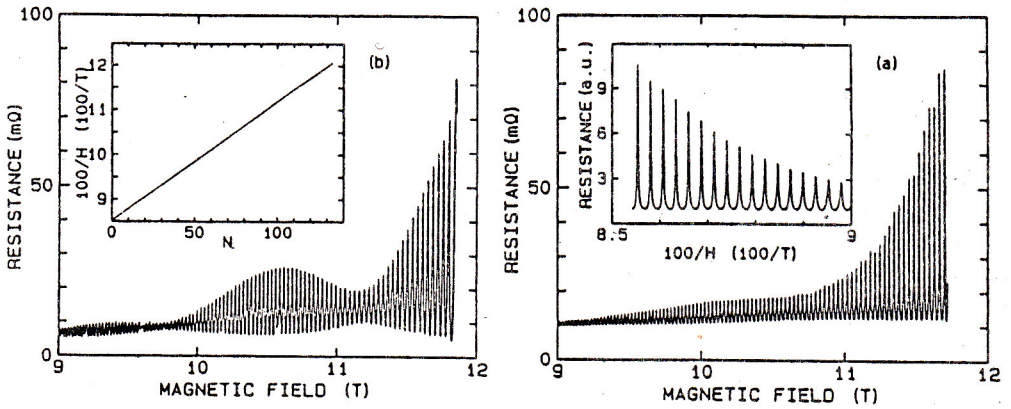

Fig.4: Magnetoresistance of β_H-$(ET)_2I_3$ between 9 and 12 T at 0.38 K and 1/H plot of the peak positions versus integer numbers (left inset). The oscillations become strongly anharmonic at highfields (right inset).

paramagnetic conducting state becomes unstable above 5T ($T \approx 0.5$ K) against the formation of an antiferromagnetic semimetal displaying a sequence of subphases. Each of these subphases is characterized by a field independent Hall voltage. Furthermore, the Hall voltage is quantized according to the law $R_H = h/Ne^2$ (N=integer). As shown in figure 3, not only are the ratios of the plateaus given by successive integers but the magnitude of the highest plateau between 14 and 18 T corresponds rather well to $h/2e^2$ = 12.9 kΩ/layer, the value expected for the quantum Hall effect (N=1) in the presence of spin degeneracy. In addition, magnetoresistance data show well defined peaks at the fields where the Hall voltage jumps to the next plateau. Above 18 T, the dramatic increase of the magnetoresistance by about four orders of magnitude suggests that the N = 0 state is attained. This state is likely to be similar to the SDW ground state observed under ambient pressure.

The ClO_4 compound behaves differently at very high fields. It exhibits a reentrance of the non-ordered phase. The ultra one dimensionalization of the electron motion under large magnetic fields may be responsible for the reentrance phenomenon of $(TMTSF)_2ClO_4$.

Other spectacular Fermi surface effects related to low-dimensionality have also been observed in the $(ET)_2X$ series. In the $(ET)_2I_3$ material superconductivity can be stabilized at T_c= 8.1 K in the β_H phase provided the cooling procedure avoids crossing a transition line below which an incommensurate lattice modulation develops[14].

Figure 4 displays giant oscillations of the magnetoresistance which exhibit a perfect (1/H) periodicity with the fundamental field H_0 = 3730 T and a beating phenomenon characterized by the much smaller field H_1 = 36.8 T[15]. The large amplitude and the beating phenomenon can both be understood in terms of a tube-like Fermi surface in a 2-D conductor. For such a situation of anisotropic surface the amplitude of the oscillations is enhanced by

the factor $(m_c/m_a)^{1/2}$, where m_c and m_a are respectively the effective mass perpendicular and parallel to the conducting planes. The beating frequency is related to the warping of the tube and thus to the interplanar coupling, namely $H_1/H_0 \alpha t_a/t_c$. For the data in figure 4 a ratio $t_a/t_c \approx 140$ is obtained. The giant magnetoresistance oscillations emphasize clearly the 2D nature of the FS of β-$(ET)_2X$ superconductors. The two dimensionality is very likely responsible for both the absence of competition between superconductivity and antiferromagnetism (as the latter instability is favoured by the nesting of quasi planar surfaces) and for the enhancement of T_c above 8K as the negative effect of fluctuations is less severe for 2-D than for Q-1-D ordering. Furthermore, band structure calculations point out that the Fermi energy of these 2-D conductors might be located close to a van-Hove singularity in the density of states. We believe that such a situation should be considered for the interpretation of the high value of T_c and for its very strong pressure dependence.

III - Conclusion

Organic superconductivity is now existing in two families of organic compounds. In the first series, $(TMTSF)_2X$, the quasi one dimensionality manifests itself first in the competition
between various ground states which is governed by parameters such as the efficiency of Coulomb interactions, the amplitude of the interchain coupling, etc.. and secondly in the remarkable field-induced spin density wave states.

The β and κ-phases of $(ET)_2X$ have proved to be two dimensional conductors after the observation of magnetoresistance oscillations which can exhibit remarkably large amplitudes in case of β-$(ET)_2I_3$.

The nature of the pairing interaction remains an open question in organic superconductors. However, the existence of strongly developed antiferromagnetic fluctuations in $(TMTSF)_2X$ materials makes a non-phonon mediated pairing mechanism quite plausible.

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