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ORGANIC SUPERCONDUCTORS : TO FLUCTUATE OR NOT TO FLUCTUATE?

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Abstract New experimental data and recent improvements of the theory suggest that the one-dimensional regime could extend much lower in temperature than what can be expected from the knowledge of band parameters. This approach allows the interpretation of the properties of $(TMTSF)_2X$ conductors which are not observed in ordinary metallic conductors and supports the existence of well developed cooperative phenomena up to 30 K.

INTRODUCTION

Approximately four years have passed since the initial observation of superconduction in a conducting organic solid. This conference comes therefore at a time which is very appropriate to check the results of research efforts developed in the field of organic superconductivity and to evaluate the possibilities for future improvments.

As this field is blooming in various directions, the present account intends to display very briefly some of the new flowers which have emerged since the last ICSM conference held in December 1982.

Superconductivity has been first observed in the single chain organic conducting salt: tetramethyltetraselenafulvalene -hexafluorophosphate [1], $(TMTSF)_2PF_6$, a member of the broader family $(TMTSF)_2X$ where X is a mineral counter-anion playing no direct role in the electron conduction which is provided by the organic molecule TMTSF [2].

In the PF_6 salt superconductivity is observed below 1 K only under a hydrostatic pressure exceeding $\simeq$9 Kbar. Important progresses in material preparation have followed shortly after the initial discovery. First, superconductivity has been stabilized in the perchlorate salt $(TMTSF)_2ClO_4$ [3] below 1.2K under atmospheric pressure. Subsequently, superconductivity has been obtained with an other organic molecule, BEDT-TTF, containing sulfur instead of selenium heteroatoms , first under pressure in $(BEDT\text{-}TTF)_2ReO_4$ [4] and subsequently at atmospheric pressure in $(BEDT)TTF)_2I_3$ [5] below 1.4 K. Recently, new phases of the (BEDT)TTF)-iodine conductor have been reported to exhibit superconductivity at atmospheric pressure below 2.5 K [6].

Besides efforts performed in the synthesis of new organic

molecules, sophisticated experimental and theoretical studies have led first to a better understanding of the electronic properties of prototype systems such as $(TMTSF)_2ClO_4$ and secondly to the observation of new and remarkable physical properties which are tightly related to the quasi-one-dimensionality of these conductors.

THE CONDUCTING STATE OF $(TMTSF)_2ClO_4$

$(TMTSF)_2X$ conductors present only one conducting chain per unit cell. The band structure is, in principle, relatively simple and practically insensitive to the temperature as long as the conducting state is stable. This feature has to be opposed to the case of two-chain conductors such as TTF-TCNQ or HMTSF-TCNQ where covalency effects between donor and acceptor chains lead to a temperature dependent band structure [7]. However, the perfect planarity of the Fermi surface of independent conducting chains is likely to be slightly modified by the existence of the non-negligible overlap between molecular wave functions belonging to molecules on near neighbouring chains. In the $(TMTSF)_2X$ structure, this is the coupling along the transverse b-direction which is relatively strong on account of short Se..Se intermolecular contacts [8].

At high temperature ($T \gtrsim 300$ K) the Fermi surface is thermally smeared over an energy interval given by $\hbar/\tau_{//}$, where $\tau_{//}$ is the intra-chain electron scattering time. Since DC and optical conductivity data give $\tau_{//} \gtrsim 3\times10^{-15}$s ($\hbar/\tau_{//} \gtrsim 0.2$ eV) the Fermi surface smearing is larger than measured or calculated values for the largest inter-chain interaction, namely $t_\perp^b \gtrsim 12$ meV [9]. Hence, the motion of electrons along b is diffusive and a metallic-like behaviour with a plasma edge around 10.000 cm^{-1} is observed only for light polarized along the high-conductivity a-axis [10]. In the high T-domain the hopping rate between chains $1/\tau_\perp$ is smaller than $t_\perp^b$ since $1/\tau_\perp \gtrsim (t_\perp^b)^2\tau_{//}$ and $t_\perp^b\,\tau_{//} < 1$, ($\hbar = 1$).

It is also the hopping rate $1/\tau_\perp$ which establishes a cut-off for the $t^{-1/2}$ 1-D time decay of the electron spin autocorrelation funciton at large times [11]. This property is particularly important in Q-1-D conductors as it enables a direct determination of $1/\tau_\perp$ via a study of the NMR relaxation rate versus the applied magnetic field [12]. When the nuclear spin-lattice relaxation is due to the hyperfine coupling of the nuclear spins to electrons moving in a given direction, $1/T_1 \gtrsim H_o^{-1/2}/\tau_{//}$ as long as $\omega_e\tau_\perp > 1$, where ω_e is the electron Larmor frequency. However at low fields if ω_e becomes smaller than a cross-over frequency ω_c ($\omega_c\tau_\perp = 1$) the usual field-independent relaxation of the 3-D regime is recovered. These properties have been studies extensively in TTF-TCNQ where the characteristic $H_o^{-1/2}$ field dependence is observed for the ^1H relaxation rate above 8 kOe. A 1-D regime ($1/T_1 \sim H_o^{-1/2}$) has been observed similarly in $(TMTSF)_2X$ conductors at 300 K but above 20 kOe [12].

The comparison between NMR data of $(TMTSF)_2X$ and selectively deuterated TTF-TCNQ leads to the following remark: $t_\perp$ in $(TMTSF)_2X$ is about twice that between TNCQ chains in TTF-TCNQ (i.e $t_\perp^b \sim 10$ meV meV in $(TMTSF)_2ClO_4$). It is interesting to recall that high-field T_1 data of HMTSF-TCNQ have failed to show any field dependence up to 60 kOe [13]. This result implies that $t_\perp$ of $(TMTSF)_2X$ cannot be much larger than $t_\perp$ in HMTSF-TCNQ, a system which undergoes a Peierls transition at 24 K [14] with high temperature precursor effects in spite of a strong corrugation of the Fermi surface. At low temperatures the thermal broadening of the Fermi surface becomes weaker and when $1/\tau_{//} \lesssim t_\perp$ (this condition should not be taken "stricto-sensu") the transverse electron motion becomes coherent. A transverse band-like behaviour is indeed observed below $\lesssim 100$ K in FIR reflectance data of $(TMTSF)_2X$ with light polarized along the b-direction [15]. The ratio of // to $\perp$ plasma edges is about 10.

Hall effect experiments performed in the low temperature conducting state of $(TMTSF)_2ClO_4$ [16] reveal a linear field dependence of the Hall voltage up to 30 kOe, also T-independent in the helium temperature range, leading to $R_H = 4 \times 10^{-9}$ m^3 /A.S. The experimental value agrees fairly well with 1-D tight binding determination in a quarter-filled band corresponding to the 2:1 stoechiometry of $(TMTSF)_2X$ salts [17], namely $R_H^{th} = 3.4 \times 10^{-9}$ m^3/AS . The low field Hall effect data strongly suggest that in spite of a somewhat important $t_\perp$ the Fermi surface of $(TMTSF)_2X$ conductors remains quasi planar with a small corrugation in the b-direction even at low temperatures.

Consequently, parallel and transverse polarized light reflectance data lead to a band structure anisotropy $t_a/t_b \sim 10$ [15]. The interchain coupling coupling in the c-direction is about one order of magnitude smaller than in the b-direction and $t_a/t_c \sim 300$. There exists much dispersion in the magnitude of t_a but the range $t_a \sim 0.12 - 0.2$ eV seems to be a reasonable compromise between experimental data and calculations.

THE 1-D REGIME IN A Q-1-D CONDUCTOR

The basis of 1-D physics is that electron-electron (Cooper) and electron-hole (Peierls) channels diverge simultaneously because of the Fermi surface invariance by a shift of wave-vector $Q = (2k_F, q_\perp)$ independent of the value of $q_\perp$ [14].

The Fermi surface warping in a real Q-1-D conductor can be neglected at high temperature as long as $T \gg t_\perp$. The response functions of the 1-D non-interacting electron gas diverge logarithmically, namely $\chi(2k_F, T) \sim \ell n \frac{E_F}{T}$. However, the two-channel mixing of the 1-D regime is stopped when $T < T_x$ where T_x is the cross-over temperature between 1-D and 3-D behaviours for the correlation functions. In a non interacting electron gas $T_x = T_x^o \sim t_\perp/\pi$ [18].

Below T_x^o the Peierls divergence levels off at $\ell n \frac{E_F}{t_\perp}$ whereas nothing prevents the Cooper divergence from continuing with a possible onset of superconductivity at T_c.

With the accepted values of $t_\perp$, T_x^o should be located around 80 K. Therefore, if the 3-D domain of the correlation functions begins at nitrogen temperature it is difficult to claim the existence of strongly developed precursors of a superconducting transition which occurs at liquid helium temperature only. Superconductivity should thus develop in a quasi-mean field way [19]. However, Bourbonnais [20] has shown that the cross-over temperature may be overestimated by, say a factor 10, not taking into account Coulomb interactions between electrons. A particular consequence of the channel mixing of the 1-D regime is the existence of long wavelength and low energy modes giving rise to:
(i) 1-D short range correlations and (ii) a depression of the single-particle density of states at the Fermi level $N(E_F)$ which reads $\sim(\frac{T}{E_F})^{2\alpha}$ where the exponent $0<\alpha<1$ depends on the interactions g_1 and g_2 in the geology model [21]. The drop in $N(E_F)$ upon cooling in the 1-D regime is also called the formation of a "pseudo-gap". Its existence has been established in the 1-D regime of 1-D conductors undergoing a Peierls transition [14].

In the vicinity of T_x^o the transfer of single particles between neighbouring chains is slowed down by the concomitant opening of the pseudo-gap. This effect has been recognized to stabilize the 1-D regime at temperatures lower than T_x^o. This means that mixed intra-chain correlations persist down to a renormalized cross-over temperature T_x which is determined by the size of the Coulomb interactions. In Bourbonnais' model [20] T_x reads $\frac{t_\perp}{\pi}(\frac{t_\perp}{E_F})^{\alpha/1-\alpha}$. As shown below $\alpha\sim0.5$ is an acceptable value for $(TMTSF)_2X$. This would extend the 1-D regime down to about 8 K since $t_\perp/E_F \sim 1/10$.

COOPERATIVE PHENOMENA IN $(TMTSF)_2X$ CONDUCTORS

A major interesting aspect of $(TMTSF)_2X$ compounds is, besides the existence of superconductivity, to know whether 1-D theories are required for their understanding or whether a band structure anisotropy of 10 is low enough to justify an anisotropic mean-field treatment for the onset of superconductivity [19]. The 3-D anisotropic model for superconductivity implies that the precursor signs of the transition develop in all three directions simultaneously. Therefore the fluctuating regime cannot be spread over more than a few Kelvin above the onset of long-range order at 1.2 K. It is important to see that this picture can be supported by some experimental data if a large amount of other results are left out. This is the case of specific heat data [22] indicating that the thermodynamics of the superconducting transition adheres rather well to a standard BCS-like model. However, the validity of an anisotropic 3-D mean-field model implies that in the T-domain 5 to 30 K the properties of the electron gas in $(TMTSF)_2ClO_4$ do not deviate significantly

from those exhibited in a regular metallic conductor at low temperature. The rest of this section is devoted to the demonstration that this is precisely not true and consequently that the conducting state of $(TMTSF)_2ClO_4$ or other members of the series below 30 K cannot be assimilated to an ordinary metallic state. We shall summarize some recent NMR results which are presented in greater details by F.Creuzet at this conference [23]. The first point we want to emphasize is that the spin susceptibility of $(TMTSF)_2ClO_4$ is both temperature and field independent below 40 K and up to 10kOe respectively [24]. Under these conditions the hyperfine spin-lattice relaxation should vary linearly with the temperature and be independent of the magnetic field (following the so-called Korringa law).

Single crystal NMR data [23] have clearly established that both properties are not followed in the R-state of $(TMTSF)_2ClO_4$:
(i) Strong enhancements above the Korringa relaxation are observed upon cooling below $\approx$25 K.
(ii) A large field dependence of $1/T_1$ is observed in the same T-domain (see figure 1 of reference [23]).

A field dependence of $1/T_1$ has also been reported for ^1H, ^{13}C and ^{77}Se nuclei in $(TMTSF)_2PF_6$ under pressure in the limited range of temperatures below 4.2 K [25]. Azevedo [25] has ascribed the field dependence of $1/T_1$ (α log H_o) to electron spins diffusing in a low dimensional conductor (2D motion). However the slope of $1/T_1$ versus $H_o^{-1/2}$ or log H_o is proportional to $1/\tau_{//}$; the inverse intra-chain electron scattering. Therefore the field dependence of $1/T_1$ should be reduced at low temperature by a factor $\approx 10^3$ below the room temperature value since the ratio of the room temperature to the 10 K resistivity reaches approximately 10^3 in good quality samples [26]. According to the known field dependence at room temperature $d(1/T_1)/dH_o^{-1/2} = 2\ s^{-1}.kOe^{1/2}$ it is impossible to attribute the important field dependence of $1/T_1$ at low temperature to low dimensional spin dynamics with the assumption of an entirely single-particle conduction below 30 K. An other interpretation has been proposed for the low temperature relaxation data [25]. The non-Korringa behaviour versus temperature can be understood in terms of a strong enhancement of the 2k SDW response at low temperature. The SDW response becomes quite significant if, for example, the 1-D regime extends down to the 5-8 K domain. As indicated in the previous section the 1-D to 3-D cross over temperature can be low if short-range Coulomb interactions are repulsive ($g_1>0$). This assumption is very plausible for the $(TMTSF)_2X$ series since:
(i) the existence of a SDW (but not CDW) state for $(TMTSF)_2PF_6$ and other members is the signature of a positive g_1 [21].
(ii) No gaps are observed in the T-dependence of the susceptibility [27].

In the presence of interchain hopping the SDW susceptibility follows a power law divergence in the 1-D regime and saturates at

T_x. In the same regime $1/T_1$ is non-Korringa. Below T_x spin-lattice relaxation tends towards another, but enhanced, Korringa regime.

The NMR studies suggest that T_x may be located in the vicinity of 5 K. This value is admittedly not far from the estimate obtained in the previous section assuming $\alpha = 0.5$ in agreement with repulsive Coulomb interactions.

As the renormalized value T_x decreases with decreasing $t_\perp$ one may expect that under large transverse magnetic fields orbital effects begin to play an important role restricting the electronic motion perpendicular to the chains [28]. This argument has been proposed [23] for the origin of the field dependence of $1/T_1$ in the 1-D regime when cooperative phenomena become predominant.

The NMR properties of the conducting state have revealed the existence of magnetic fluctuations at low temperature in $(TMTSF)_2ClO_4$, R-state. However, in the 1-D regime, magnetic fluctuations may coexist with superconducting precursor effects since the coupling between electron-hole and pairing correlations is the heart of 1-D physics. We shall briefly recall some experimental data related to transport and density of states properties which are hard (if not impossible) to understand within the framework of a gas of single-particles.

DC conduction becomes extremely large at low temperature ($\sigma(2K) \gtrsim 10^6 (\Omega cm)^{-1}$) in $(TMTSF)_2ClO_4$ with an anomalously strong sensitivity to the application of a transverse magnetic field [29].

The high conductivity is restricted to a narrow mode at zero frequency. Its width, derived from FIR reflectance studies, is about <0.5 cm^{-1} at 2 K [30]. Furthermore, Timusk et al [31] have shown that it is impossible to fit the frequency dependence of the conductivity in the FIR regime by a Drude-like behaviour. Finally, as more and more electron states near the Fermi surface couple to build up (in the 1-D regime) the long wavelength low energy collective mode, the density of states at the Fermi level becomes depressed (formation of a pseudo-gap). This phenomenon is probably responsible for the "gap" observed in the FIR conductivity below 30 cm^{-1} [30].

The pseudo-gap formation could also explain the behaviour of recent tunneling data of electrons in lead (superconducting)-insulator-$(TMTSF)_2ClO_4$ junctions between 5 and 1.2K [32]. Junctions of high quality reveal a smearing of the typical BCS singularities at the lead gap edges. This effect is pretty well understood by a tunneling response being the convolution between the ordinary N(E) of superconducting lead and the density of states of $(TMTSF)_2ClO_4$ showing a pronounced depression over an energy width of about 3.6 - 3.8 meV.

The anomalous drop of the thermal conduction at low temperatures [33] has also been related to the joint formation of a DC collective mode contributing to the electron transport (but not to heat transport) and of the pseudo-gap in the single-particle density of states.

CONCLUSION

Progresses in the theory have shown how One-Dimensionality can be stabilized at low temperatures by 1-D correlations in a 1-D Coulomb electron gas. This model reconcile the numerous anomalous features of the NMR observed below 30 K with the modest band structure anisotropy of 10.

It is clear that the theory of Q-1-D superconductors will require further improvements, but we feel confident that a Landau-Ginzburg treatment of the order parameter phase fluctuations close enough to T_c, when Peierls and Cooper channels become decoupled [34], constitute a reasonable starting point. Such a picture has the merit to reconcile the quasi BCS behaviour of the superconducting transition itself with the existence of a broad fluctuation domain.

Other data require 1-D physics for their interpretation. It is, for instance, the case of the interplay between magnetism and superconductivity observed in all $(TMTSF)_2X$ superconductors [35] and the stabilization of a SDW semimetallic 2D state (in terms of Fermi surface topology) under high transverse fields [36,37]. This latter aspect has led to spectacular developments also related to the Hall quantization which are also presented at this conference [26,38,39]. A crucial question is still left without answer: it is adressed to the nature of the pairing (spin singlet or triplet) in the 3-D superconducting state as well as in the precursor regime. There are no, so far, direct evidences showing triplet pairing besides the remarkably strong sensitivity of organic superconductivity to traces of non-magnetic impurities and the g-ology model which favours triplet pairing when g_1 is positive [35].

Similarly, a correct treatment of the fluctuation conductivity has to be developed; especially under high field where the model of Efetov [40] would require some modifications to be adapted to the $g_1>0$ situation.

In conclusion, the results presented at this conference show that on several points the ideas about Q-1-D organic superconductors are converging, for ex, role of Coulomb interactions on the definition of the 1-D regime, SDW state at high field, FIR conductivity, etc...More effort in chemistry is still needed to improve materials properties as far as superconductivity is concerned. This seems to be "conceptually" feasible.

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