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Impurity controlled Superconductivity/Spin Density Wave interplay in the organic superconductor : $(TMTSF)_2ClO_4$

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Abstract. – The study of the anion ordered $(TMTSF)_2ClO_{4(1-x)}ReO_{4x}$ solid solution in the limit of a low ReO_4^- substitution level ($0 \leq x \leq 17\%$) has revealed a new and interesting phase diagram. Superconductivity is drastically suppressed as the effect of ReO_4^- non magnetic point defects increases following the digamma behaviour for usual superconductors in the presence of paramagnetic impurities. Then, no long range order can be stabilized above 0.1K in a narrow window of substitution. Finally, an insulating SDW ground state in ReO_4^--rich samples is rapidly stabilized with the decrease of the potential strength leading to the doubling of the transverse periodicity. This extensive study has shown that the superconducting order parameter must change its sign over the Fermi surface.

The symmetry of the superconductivity order parameter remains a controversial question in organic superconductors where unlike the high T_c cuprates phase sensitive experiments have failed so far to provide a clear cut answer [1]. Among the various experimental approaches used to tackle the problem of the order parameter symmetry the sensitivity of the superconducting state to non magnetic impurities is known to be quite pertinent since unlike conventional s-type superconductors, unconventional superconductors, singlet d [2] or triplet p or f type [3–6] are strongly affected by their presence. Organic superconductors belonging to the $(TMTSF)_2X$ family of one-dimensional conductors [7] provide a situation which is very well adapted to the study of the role of non magnetic impurities on the superconductivity instability. The solid solution $(TMTSF)_2ClO_{4(1-x)}ReO_{4x}$ which has been the subject of an exhaustive crystallographic study [8] represents a very good example since a small amount of ReO_4^- anions does not disturb the electronic structure and yet profoundly affects the stability of the superconductivity phase of the pure $(TMTSF)_2ClO_4$ compound [9,10]. A preliminary study of $(TMTSF)_2ClO_{4(1-x)}ReO_{4x}$ has been carried on previously [11] but it was restricted to the low dilution regime namely ≤ 6 %. It was shown, plotting the value of T_c versus the residual resistivity of the normal state that the strong suppression of T_c does not support the existence in these organic superconductors of an order parameter keeping the same sign over the entire Fermi surface. The present work extends the investigation towards higher concentrations of ReO_4^- anions. Furthermore, a reinvestigation of the procedure used for the plot of

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T_c *vs* ρ_0 has been performed leading to removing some flaws in the previous interpretation [11]. In addition, we have studied the solid solution up to x=17 % showing that after the suppression of the SC phase there exists a narrow window in the impurity doping where no low range order can be stabilized at low temperature. At larger doping an insulating spin density wave (SDW) ground state becomes stable. Sample growing and measurements of the resistivity along the c* axis (weakest conductivity direction) have been performed following a procedure mentioned previously [11]. As done before, the elastic electron life time of the normal state has been characterized by the residual term derived in a polynomial fit of the resistivity *versus* temperature in the metallic state. We have clearly identified a temperature regime above the superconducting transition in which precursor superconductivity is dominant over the more conventional behaviour prevailing at higher temperatures. Consequently,*at variance* with the procedure used earlier which was based on a linear extrapolation of the temperature dependence of the resistivity below 10 K we have extracted the value of ρ_0 from the quadratic temperature dependence which is observed above 10 K. Hence, the previous use of a linear law to extract the value of the residual resistivity leads to a serious underestimation of ρ_0. We think that the present approach is more appropriate to the picture of a Fermi liquid which can be expected to hold at low temperature in these quasi 1 D conductors.

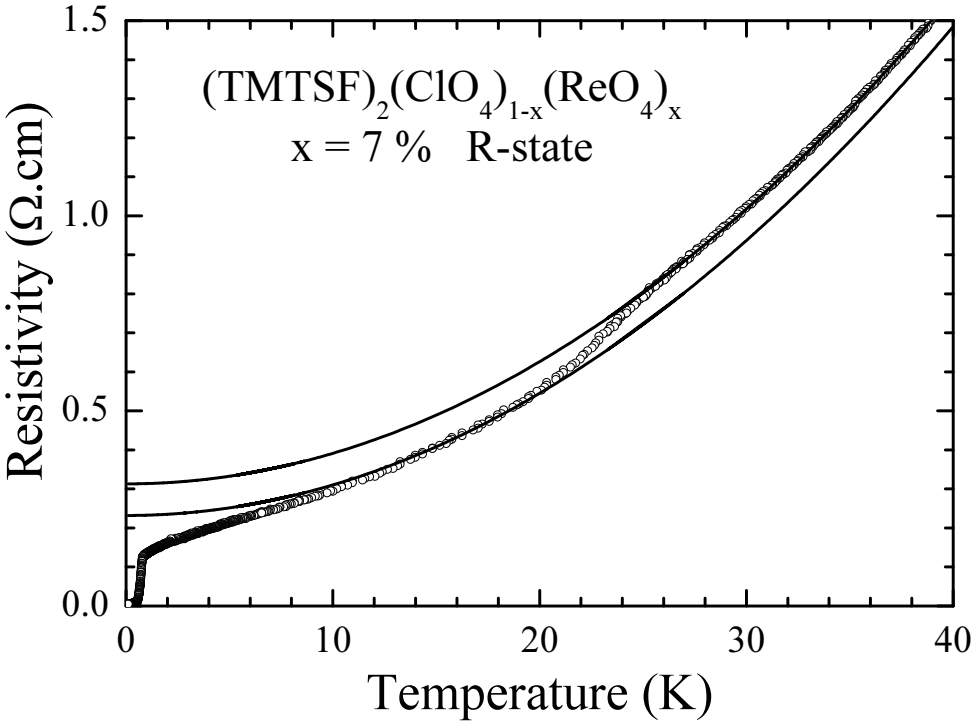

Fig. 1 – Temperature dependence of the resistivity in $(TMTSF)_2ClO_{4(1-x)}ReO_{4x}$ showing the T^2 law obeyed with the same value of the prefactor A on both sides of the anion ordering transition . The ordering amounts to a decrease of the elastic scattering. The temperature dependence departs from the T^2 behaviour in the precursor superconductivity regime below 10K or so.

Figure 1 displays the temperature dependence of the resistivity ρ_c plotted against T below 40K. The anomaly noticed at 24 K corresponds to the well known ordering of the tetrahedral anion ClO_4^- leading to additional Bragg reflections [12] at a wave vector (0,1/2,0) and con-

comitantly to a reduction of the elastic electron scattering in the ordered phase below T_{AO}. It can be noticed that a quadratic law is well obeyed above T_{AO}. This behaviour is understandable since the T^2 term is the signature of electron-electron scattering in the Fermi liquid with the prefactor A determined by the density of states at the Fermi level *albeit* possibly enhanced by correlations. The onset of the anion ordering amounts to a folding of the energy dispersion along the b-direction which should not affect $N(E_F)$ and hence the magnitude of the electron-electron scattering. Below T_{AO} a quadratic law is also followed with the same prefactor A within the accuracy of a fit which can only be performed in a narrow temprature domain while the constant term ρ_0 is diminished. In the present work it is the value of the residual resistivity ρ_0^- derived from the quadratic low below T_{AO} which has been used as the parameter describing the amplitude of the elastic scattering rate when non magnetic impurities are added to those present initially in the pure compound. On figure 2 the value of T_c obtained either from the onset of superconductivity in the ρ(T) data or equivalently from the temperature where H_{c2} reaches a zero value has been plotted versus ρ_0^- for the different solid solutions. For all samples, the so-called relaxed state (R) at low temperature has been obtained with a slow cooling rate of -0.05K/mn (-3K/hour) below 30 K, (in some cases shown in the figure, faster cooling rates have also been used). We may notice that the amount of disorder in a sample is better characterized by the residual resistivity ρ_0^- than by its nominal impurity concentration given by chemistry. This can be ascribed to the impurity distribution existing in every batch. As displayed on fig.2, all T_c data fit with a very good accuracy the life time dependence given by the digamma function [4, 13],

$$ln(\frac{T_{c0}}{T_c}) = \Psi(\frac{1}{2} + \frac{\alpha T_{c0}}{2\pi T_c}) - \Psi(\frac{1}{2}) \quad (1)$$

with Ψ being the digamma function, $\alpha = \hbar/2\tau k_B T_{c0}$ the depairing parameter and τ the elastic scattering time.

According to fig2 the virtual critical temperature in the absence of any scattering amounts to 1.57 K. Pristine $(TMTSF)_2ClO_4$ samples although pure enough to exhibit superconductivity between 1.20-1.30 K are still far from perfect purity. What is remarkable in the data of fig.2 is the existence of a highly ReO_4^-substituted sample (10%) which has provided different values of T_c depending on the cooling rate. These data lie precisely in the regime where the digamma function departs from the linearity *versus* $1/\tau$. At higher impurity content, (x=15%) a new behaviour has been observed. The anions still order below T_{AO} still of the order of 24K as indicated by the concomitant drop of the residual resistivity (although smaller than what is observed in purer samples). An upturn of the resistivity noticed at low temperature in the R-state can be ascribed to the onset of an insulating ground state at 2.35 K (as defined by the maximum of the logarithmic derivative of the resistance *versus* T).

We may relate the onset of an insulating ground state to the occurence of SDW modulation as also checked by EPR experiments either in the R-state of ReO_4^-- substituted samples [14] or in rapidly cooled samples [14, 15]. The SDW temperature of the 15 % sample is about half the value of $T_{\rm SDW}$ obtained in rapidly cooled samples (Quenched-state). The case of the 15 % sample can be understood in terms of the model showing how the anion ordering can lower the SDW stability. It has been shown that the stability of a SDW ground state in the R-state of $(TMTSF)_2ClO_4$ can be strongly suppressed by the additional transverse potential introduced in the ordered state below T_{AO} [16].

What is also remarkable in the interplay between SC and SDW as shown in fig.2 is the existence of a range of impurity concentrations illustrated by the 8% sample in which neither SC nor SDW phases can be stabilized down to 100 mK. Such a behaviour is *at variance* with the existence of a common border between SDW and SC in the T-P phase diagram of the

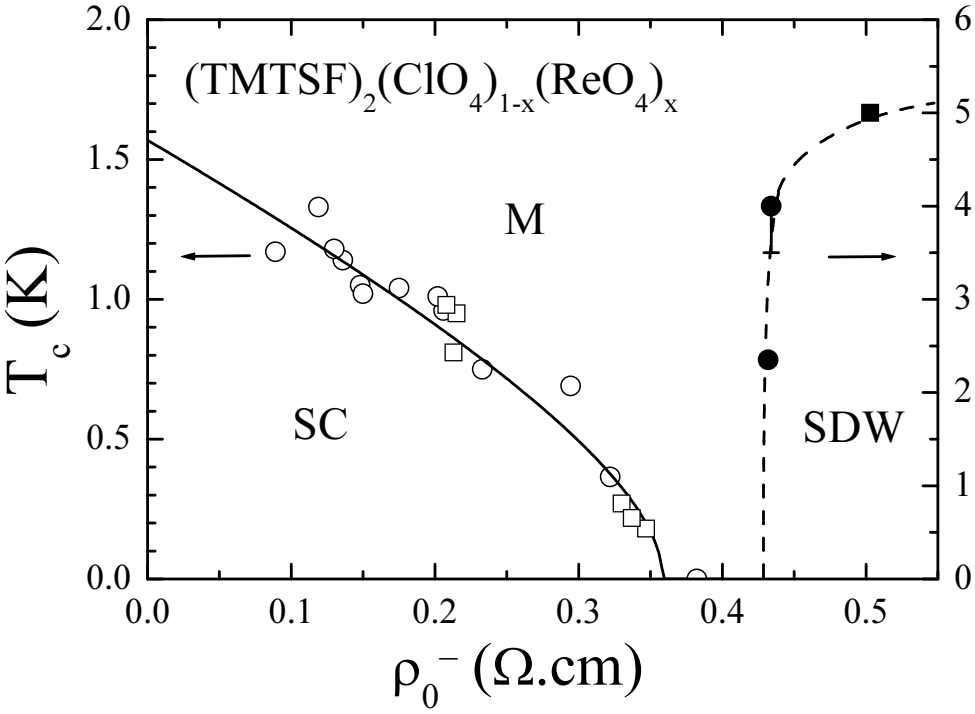

Fig. 2 – Phase diagram of $(TMTSF)_2ClO_{4(1-x)}ReO_{4x}$ governed by non magnetic disorder. All open circles refer to the very slowly cooled samples in the R-state with different ReO_4^- contents. Open squares are data for the same samples corresponding to slightly larger cooling rates although keeping a metallic behaviour above T_c. The 10% sample with $\rho_0^- \approx 0.32\Omega$.cm has provided four different T_c depending on the cooling rate. One sample (8%) did not reveal any ordering down to 0.1K. These data show that the residual resistivity is a better characterization for the disorder than the nominal ReO_4^- concentration. Full dots (15 and 17%) are relaxed samples exhibiting a SDW ground state. The vertical bar is the error bar for a sample in which a maximum of the logarithmic derivative could not be clearly identified and therefore the actual SDW temperature should lie below 4K, the temperature of minimum resistivity. The full square is the Q-state of a 6% sample. The continuous line at the M-SC transition is the best fit of the data with the digamma function providing $T_{co} = 1.57$K. The dashed line at the M-SDW transition is a guide for the eye.

parent superconductor $(TMTSF)_2PF_6$. However, as far as the latter compound is concerned impurities are not involved in the pressure dependence of the superconducting state and the maximum T_c is located at the common border between SDW and SC.

The good agreement between the experimental dependence of T_c *versus* the elastic scattering and the theory of the limitation of T_c by non magnetic impurities in unconventional superconductors is strongly suggestive of an homogeneous material where the ClO_4^- anions are ordered and ReO_4^- anions play only the role of point defects.

However, quite a different behaviour for the interplay between SC and SDW is observed when the cooling rate is increased in a sample of a given composition. As shown in fig.3a for a pristine sample in the limit of the low cooling rates the critical temperature decreases gently at increasing rates with a concomitant increase of the residual resistance following the digamma behaviour. We can ascribe this regime to the limit where the disordered anions play the role of point defects in an homogenous sample and destroy the superconducting state in

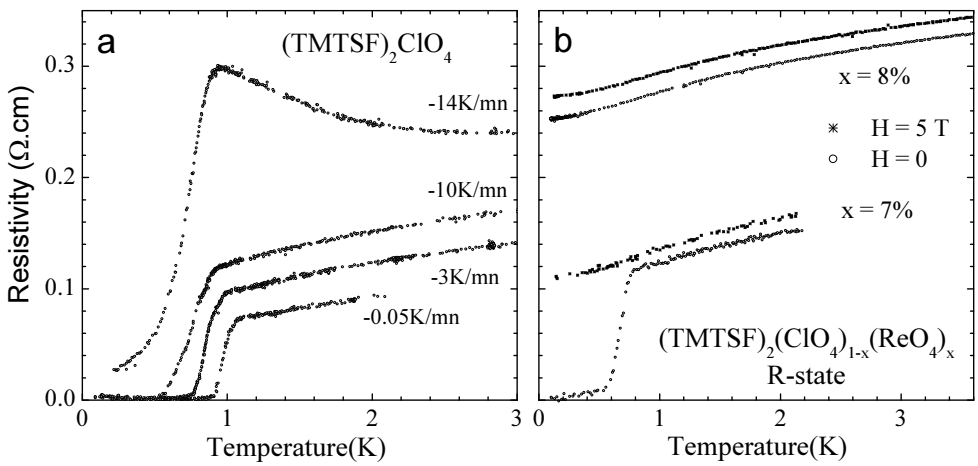

Fig. 3 – (a) Evolution of the resistive behaviour in pure $(TMTSF)_2ClO_4$according to the cooling rate. (b) Persistence of the presursor regime in impure samples and under magnetic fields larger than the critical fields.

a way similar to the alloying effect. However, when the cooling rate overcomes say, -3K/mn a violation of the digamma behaviour is clearly observed (not shown on fig. 2). While ρ_0^- keeps increasing with the cooling rate, T_c stays constant at about 0.8K . In addition, for a rate of -14 K/mn a superconducting signature is observed at 0.8 K below a weak upturn of the resistivity at 2.5 K.

These data can be understood assuming the low temperature phase is becoming inhomogeneous at fast cooling rates. A possible scenario is the occurence of macroscopic coherence via Josephson coupling between superconducting islands in which the anions are fairly well ordered (double sheeted Fermi surface) separated by regions in which only short range order prevails in agreement with the X-rays determination of the correlation length in quenched samples [17] . In the latter non-metallic regions $T_{\rm SDW} = 2.5$ K is lower than the SDW temperature which is observed for a fully Q-state ($T^{\rm Q}_{\rm SDW}$= 5 K) with a single-sheeted Fermi surface. Furthermore, on account of the loss of the density of states at the Fermi level below $T_{\rm SDW}$ no superconductivity can be stabilized in those domains which in turn remain insulating at low temperature. The evolution of the transport properties corroborates the specific heat study which has been performed in $(TMTSF)_2ClO_4$ varying the cooling rate [18]. From the reduction of the entropy involved in the SC transition it was concluded that for a cooling rate of -10K/mn the low temperature state of the sample might contain some proportion of SDW phase. The response of the transport properties to the cooling rate has also been observed in the ReO_4^-- doped samples but in this case the presence of point defects (ReO_4^-anions) slows down the dynamics of ordering. Consequently, in highly doped samples an inhomogeneous behaviour can more easily be attained even for low cooling rates .

We shall now address the problem of the downturn of the resistivity which is clearly observed below 10K down to the superconducting transition, (see fig.1). Such a behaviour is quite general since it had already been reported in the discovery of superconductivity of $(TMTSF)_2PF_6$ [19] and $(TMTSF)_2ReO_4$ [20] under pressure. This downturn is robust against the presence of impurities and also against the application of a large magnetic field, fig.3b. As far as the data of fig.3b are concerned it is important to notice that the field induced spin density phases which should be present at low temperature in a field of 5 T //c

are suppressed by impurities although they may possibly occur at a higher field [21]. The theoretical basis for the downturn of the resistivity has already been debated in the past [22] with no common consensus reached [23, 24] and it will be the subject of a forthcoming publication. It was claimed that the behaviour of the resistivity could be interpreted as precursors to the superconducting ground state with large fluctuations around a mean field transition temperature of (10-15K) within the framework of existing band structure calculations [22].

Without entering this controversy again some new experimental data of the present study should be emphasized. Since the downturn of the resistivity is still observed under experimental situations where superconductivity is suppressed either by non magnetic impurities or by a magnetic field of about 8 times the critical field along the c-axis (see, fig.3b) we may rule out the possibility of paraconductive fluctuations over a temperature domain extending up to 10K or so. Furthermore, fluctuations of a SDW contributing to a collective mode seem unlikely because first, they would be pinned by strong commensurability effects and second, there are no signs of magnetism in the low temperature conducting phase of relaxed samples. We wish to propose a possible scenario already suggested in the context of the high T_c cuprate materials namely, the existence of a pseudogap with an inelastic scattering rate becoming shorter in the pseudogap regime [25]. A charge pseudogap has been identified by tunnelling spectroscopy either in $(TMTSF)_2ClO_4$ [26, 27] or in $(TMTSF)_2PF_6$ under pressure [28] with an approximate width of $2\Delta \approx 2 - 3meV$. Even if the pseudogap is not due to an incoherent superconducting pair formation below a high mean field temperature it can still be due to fluctuations of an other type namely, antiferromagnetic fluctuations which have been detected by NMR relaxation experiments [29]. Consequently, the picture of these organic superconductors bear some similarity with the underdoped regime of high Tc's where both a departure of the resistivity from the high temperature linear behaviour is observed and magnetic fluctuations have been identified by NMR.

The study of the solid solution $(TMTSF)_2ClO_{4(1-x)}ReO_{4x}$ in the limit of a low ReO_4^- substitution level ($x < 17\%$) has revealed a new and interesting phase diagram once the ordering of the tetrahedral anions is achieved below 24K. The insulating SDW ground state of ReO_4^--rich samples is quickly suppressed with an increase of the amplitude of the anion potential doubling the transverse periodicity. Then, no long range order can be stabilized above 0.1K in a narrow window of substitution and at lower substitution level the stabiblity of a superconducting ground state grows as the system evolves towards pure $(TMTSF)_2ClO_4$. We are in the presence of a SDW/SC interplay of quite a different nature than the usual interplay observed in $(TMTSF)_2PF_6$ under pressure. In the present case, SC and SDW are decoupled phenomena as illustrated by the gap between these two instabilities in fig. 2 whereas the stability of superconductivity in $(TMTSF)_2PF_6$ is in close relation with the SDW state. The main factor governing the stability of the superconducting state in $(TMTSF)_2ClO_{4(1-x)}ReO_{4x}$ and in turn its T_c is the elastic electron lifetime and not the band and correlation parameters. This extensive study has shown that the order parameter has to change sign over the the Fermi surface.

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