INFLUENCE OF THE DISORDER POTENTIAL OF THE ANIONS ON THE GROUND STATE OF THE ORGANIC ALLOY (TMTSF)$_2$(C$_{10}$)$_{1-x}$(ReO$_4$)$_x$

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Résumé - Nous présentons une étude expérimentale de l'alliage organique (TMTSF)$_2$(C$_{10}$)$_{1-x}$(ReO$_4$)$_x$. Les résultats montrent l'influence importante des impuretés non-magnétiques sur le comportement à basse température.

Abstract - We present experimental investigation of the organic alloy (TMTSF)$_2$(C$_{10}$)$_{1-x}$(ReO$_4$)$_x$. The results show an important influence of nonmagnetic impurities on a low temperature behaviour.

We report an experimental investigation of the organic alloy (TMTSF)$_2$(C$_{10}$)$_{1-x}$(ReO$_4$)$_x$ including EPR and electrical conductivity measurements. This work is continuation of our previous investigation of the influence of the anion disorder on the low temperature (LT) behaviour of (TMTSF)$_2$C$_{10}$$_4$ (1). A priori we expect that doping ReO$_4$ into (TMTSF)$_2$C$_{10}$$_4$ have two effects: I it influences the ordering temperature of the anion lattice (22 K in pure (TMTSF)$_2$C$_{10}$$_4$) and the relative stabilities of the R and Q-states, and II even in the R state which is metallic and superconducts below 1.3 K in pure (TMTSF)$_2$C$_{10}$$_4$ the small modulation of the anion potential (ReO$_4^-$ is slightly larger and may exhibit different charge-distribution) should influence not only the amplitude and phase coherence of the SC order parameter, but also the coherence length along the chains. The effect of doping the organic stack was already evaluated by several authors, most recently by C. Coulon et al. (2) who examined the effects of doping (TMTSF)$_2$C$_{10}$$_4$ with TMTTF.

RESULTS

Materials were prepared by electrochemical oxidation of TMTSF in THF containing n-BA C$_{10}$$_4$ and Re$_4$ in appropriate ratio. The content of Re$_4$ refers to the composition of the stack solution because the detailed analysis of homogeneity and actual Re$_4$ content is not yet finished.

EPR results are given in Fig. 1 and Fig. 2.

The R-state is obtained by slow cooling below 30 K at a rate of about 10 K/h (∼ 5 K/h for x = 0.17). The Q-state is obtained by rapid cooling below 30 K by a rate ∼ 3 x 10$^4$ K/h. Fig. 1 shows the temperature dependence of the intensity and the linewidth of the field derivative of the absorption EPR signal. In Fig. 2 results of the annealing experiments performed as described elsewhere (1) are given. We have analyzed the data according to the expected effects.

ad.I We observe two features: First, the transition temperature $T_A$ is decreasing as the impurity concentration (x) is increased. $T_A$ is 22 K for pure (TMTSF)$_2$C$_{10}$$_4$ ∼ 18 K for x = 0.01 and ∼ 17 K for the x = 0.05 alloy. For x = 0.17 only partial A$_0$ is established. Secondly, much longer time ($t_{ann}$) is necessary to anneal disorder frozen in in the lattice by rapid cooling. According to the EPR intensity $t_{ann}$ is

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Fig. 1
Normalized EPR intensity $I/I_R$ and linewidth $LW$ versus temperature $T$ in the R and the Q-state. $I_R$ is the intensity in the R-state.

Fig. 2
Normalized intensity $I/I_R$ and linewidth $LW/LW$ versus the annealing temperature for different annealing times $\tau_{ann}$ measured at 3.7 K. Schematic diagram of the annealing experiments is given in insert.
**Fig. 3**

Normalized conductivity versus temperature in the R-state obtained by slow cooling below 30 K.

**Fig. 4**

Logarithm of normalized resistivity versus inverse temperature in the R- and the Q-state.
ranging from \( \sim 15 \) sec (at \( T_{A0} \)) for pure \((\text{TMTSF})_2\text{ClO}_4\) up to \( \sim 60 \) min for \( x = 0.17 \).

Ad. II (referring mainly to R-states). Conductivity results are given in Fig. 3 and Fig. 4. For \( x = 0.01 \) there is still a transition to a superconducting state at \( T_{sc} \sim 0.9 \) K as determined by a Meissner effect experiment. For higher concentrations \( x = 0.05 \) and \( x = 0.17 \) we fail to observe SC down to \( \sim 0.1 \) K.

**DISCUSSION**

The proposed \( T-x \) phase diagram is given in Fig. 5.

![Fig. 5 - Proposed x (impurity concentration) versus T (temperature) phase diagram for the R and the Q-state of the organic alloy \((\text{TMTSF})_2(\text{ClO}_4)_{1-x}(\text{ReO}_4)x\).](image)

- **Q-state** - The properties \( (\chi_{\text{EPR}}) \) do not appear to depend strongly on the impurity concentration. Below about 7 K the EPR line broadens and below about 4 K the susceptibility becomes vanishingly small as in pure \((\text{TMTSF})_2\text{ClO}_4\).

  This strongly indicate that the Q-state in the alloys, as in the pure material, has SDW character.

- **R-state** - In contrast, the properties of the R-state are more sensitive. Already at low levels \( (x = 0.01) \) the conductivity saturates below 3 K, whereas the magnetic properties are very similar to those of the pure compound.

  We also note that \( x = 0.01 \) is sufficient to shift \( T_{sc} \) from 1.3 K to 0.9 K. For \( x = 0.01 \) one nominal defect per hundred lattice constants is probably less efficient in affecting the coherence along chains, than in affecting the phase coherence of the SC order parameter between chains. For \( x = 0.05 \) and 0.17 we notice although the anions are probably ordered (only partially for \( x = 0.17 \)) there is no enhancement of the conductivity below about 20 K. Below 4 K and 5.5 K for \( x = 0.05 \) and 0.17 respectively we notice a decrease in conductivity and SC is suppressed at least to below 0.1 K (exp. limit). Whether the upturn arises from onset of SDW or another mechanism is operating is unclear since we only for \( x = 0.17 \) observe the expected drop of \( \chi_{\text{EPR}} \) (3.6 K is exp. limit).

  We do, however, emphasize that already at \( x = 0.05 \) a disorder potential is strong enough to prevent a SC ground state to be created. Recall that in pure \((\text{TMTSF})_2\text{ClO}_4\) only very fast quenching completely suppressed SC (4), while a variety of mixed states were also observed at intermediate rates. Note also an apparent maximum LW in the R-state in the \( x = 0.05 \) alloy. In the \( x = 0.17 \) alloy the linewidth again narrows and approach that of the Q-state. This maybe due to a change of efficient dimensionality when the dopant concentration increases, whereas the narrow line in the pure system is probably due to a very high conductivity.

  The main result of the present work is that impurities are very efficient in suppressing superconductivity. In the \( \text{ClO}_4\)-\( \text{ReO}_4 \) alloys, it is important to point out that the impurities have several effects.

**I.** Low levels suppress SC and probably give rise to the competing SDW phase in analogy with quenching in the pure system (1,5).

**II.** Even although the SDW phase can be suppressed by moderate pressures and a metallic behaviour reappears, SC is not observed \( (x = 0.17, p = 5 \) kbar\). This latter result indicate that \( \text{ReO}_4 \) impurities are also efficient in limiting the coherence length along the chain. It appears that II is the most important effect because in pure \((\text{TMTSF})_2\text{ClO}_4\) even although the SDW state appears in the M-states (which apparently have similar SDW amplitude as for example the 0.05 alloy) SC can still be observed.
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