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COMPETITION BETWEEN SDW AND SUPERCONDUCTIVITY IN $(TMTSF)_2X$ COMPOUNDS

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The phase diagram of a quasi-one-dimensional metal with retarded and nonretarded forward and backward scattering is derived. It is shown that singly charged acceptor molecules produce a potential along the conducting chains which leads to umklapp scattering. This umklapp scattering depends strongly on the phonon frequency and can explain the crossover from spin density waves to superconductivity as observed in the $(TMTSF)_2X$ compounds. The relevance of recent magnetoresistance measurements to the proposed model is discussed.

1. INTRODUCTION

In principle there are four possible types of order in a one dimensional metal as $T \to 0$: charge density waves (CDW), spin density waves (SDW), and singlet and triplet superconductivity (SS and TS). The underlying physical picture, which has been the cornerstone of the theorist viewpoint of one-dimensional metals is the phase diagram of an electron system with forward and backscattering. On the basis of this picture, the competition between the different types of order and the possible crossover from one type of behaviour to another by external means, like pressure or irradiation, were discussed extensively in the literature. In our previous work on the subject, we put particular emphasis on the competition between CDW and SS, and the possibility of superconductivity as a

result of suppression of the competing charge density wave instability by the application of pressure.

The interest in the possible phase transitions in quasi-one-dimensional metals was enhanced by the discovery of the $(TMTSF)_2$ X class of "monochain" compounds in which only the donor chains of the TMTSF molecules participate in the electron transport[1]. In several compounds of this class a crossover from an insulating to a superconducting state was observed under pressure. The prototype compound of this class is $(TMTSF)_2 PF_6$, which has a metal-insulator transition at ambient pressure around 12^oK and becomes superconducting around 1^oK above 12 Kbars [2,3,4]. (In ref. 4 superconductivity was observed at 6.5 Kbar.). The most striking novel feature of these compounds is that their insulating state is a SDW[5], rather than a CDW as in the other organic metals.

In the present paper we shall first briefly review our previous work on the competition between superconducting and insulating phases in 1-d metals. The new features of the $(TMTSF)_2$ X compounds require some modifications of previously developed picture. In particular the inclusion of retardation effects and umklapp seems to be essential. When this is done, a natural explanation of the behaviour of these compounds emerges[6]. The main part of this paper is devoted to these later developments.

2. THE g-OLOGY PICTURE

The main feature of the 1-d metals is the simultaneous divergence of the electron-electron and electron-hole propogators. The first divergence occurs also in a 3-d system and it indicates the onset of Cooper pairing, which could be either singlet or triplet. The second divergence occurs in a system with a nested Fermi surface, namely, when $\varepsilon(\underline{k}) = -\varepsilon(\underline{k} - \underline{q}_o)$ for some q_o and all $\underline{k}$ at the Fermi surface. This is a property of a 1-d system, and it indicates the onset of singlet (CDW) or triplet (SDW) electron-hole pairing. The co-existence of divergencies leading to competing types of order was first discussed by Bychkov et al[7].

In a strictly 1-d system there are no real phase transitions and the meaningful question in this case is: what is the type of order at T = 0 ? In order to discuss a more realistic model one has to introduce some interchain coupling. Coulomb interaction between the chains favors CDW and is not sufficient to stabilize a 3-d transition at finite T for the other types of order[8]. To this end one needs interchain tunneling. We have previously adopted, and discussed

extensively in various contexts, a model in which the interchain tunneling is represented by the electron dispersion[9]

$$\varepsilon(k) = \varepsilon(k_z) - t_\perp (\cos ak_x + \cos ak_y), \qquad (1)$$

where $t_\perp$ is the interchain transfer integral, a - the interchain distance, and $\varepsilon(k_z)$ is a free electron dispersion along the chains. The deviation from one-dimensionality is characterized by the value of $t_\perp$, and the interesting range of values is

$$4T_P < t_\perp < 3(T_P T_F)^{1/2}, \qquad (2)$$

where T_P is the Peierls transition temperature for $t_\perp = 0$ and T_F is the Fermi temperature. The upper limit assures that the system is not too 3-dimensional so that there is sufficient nesting (the nesting vector is $q_o = (\pi/a, \pi/a, 2k_F)$ for the possibility of the insulating phases to occur. The lower limit assures that the system is not too 1-dimensional so that mean-field-theory would apply. Moreover, the Cooper channel and the Peierls channel are decoupled for these values of $t_\perp$, and the most divergent set of diagrams reduces to that of the Hartree-Fock scheme for each type of order separately.[10]

With nonretarded interactions, this scheme leads in weak coupling limit to the phase diagram[11] shown in Figure 1.

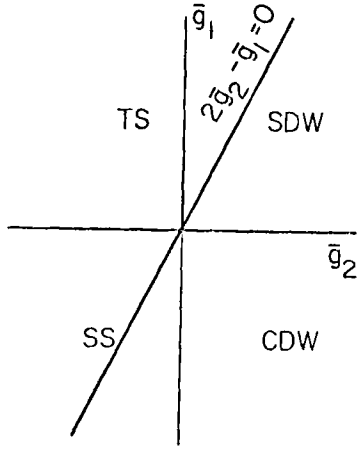

FIGURE 1 Phase diagram of 1-d metals based on mean-field theory.

The main feature of this diagram is the separation between superconducting and insulating phases by the line $\bar{g}_1 = 2\bar{g}_2$, and between singlet and triplet phases by the line $\bar{g}_1 = 0$, ($\bar{g}_2$, $\bar{g}_1$ are the forward and backward scattering amplitudes measured in units of the bandwidth).

3. PHASE DIAGRAM FOR THE FROHLICH HAMILTONIAN

One of the advantages of the mean-field approach is, that one can include explicitly phonons and the retardation effects associated with their interaction. The model based on eq.(1) was applied to investigate the phase diagram of an electron-phonon system described by the Frohlich Hamiltonian(without Coulomb interactions). In this case $\bar{g}_1$, $\bar{g}_2 < 0$, and one finds a competition between superconductivity and the Peierls transition. To distinguish between the Coulomb, nonretarded, interactions and the phonon induced electron-electron interactions, we shall denote the latter by λ_1 and λ_2 (for the backscattering and forward scattering, respectively). Note that, $\lambda_i = G_i^2 N(0)/\omega_o$ where G_i is the Frohlich electron-phonon coupling constant, for $q = 0$ ($i = 2$) or $q = 2k_F$ ($i=1$) phonons, and ω_o is the phonon frequency (assumed here to be constant).

The transition temperature T_S and T_P, for these instabilities were calculated by solving the coupled Eliashberg equations in both channels [10,12] and the results are summarized in Fig. 2a,b. Fig. 2a plots T_P and T_S as a function of $\lambda = \lambda_1 = \lambda_2$ for several values of ω_o/E_C. Except for the nonretarded case (C), there is a critical coupling above which $T_P > T_S$, and below which $T_S > T_P$. This crossover from the Peierls instability to BCS-pairing when λ is reduced, is demonstrated again in Fig. 2b which shows the borderlines between these instabilities in the ($\bar{g}_1$, $\bar{g}_2$) -plane. In general one finds that for a given λ_2 the maximum value of T_S varies from $\omega_o/50$, for weak λ_2, to $\omega_o/20$, for strong λ_2. The same qualitative result was derived previously[13] by assuming that the coupling constant λ depends on T because of the phonon softening due to the Kohn anomaly.

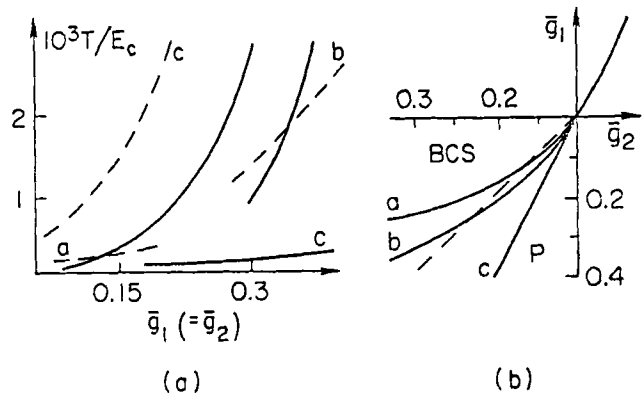

FIGURE 2 (a) Solutions of Eliashberg eqs. for T_p (solid lines) and T_s (broken lines) for $t_\perp = 0.1E_F$ and $\bar{g}_1 = \bar{g}_2$.
FIGURE 2 (b) Boundary lines between BCS and Peierls regions. Broken line corresponds to $\bar{g}_1 = \bar{g}_2$.
In both figures: a) $\omega_o/E_c = 0.1$; b) $\omega_o/E_c = 0.3$; c) $\omega_o/E_c \to \infty$.

This picture was the basis for the discussion of the possible effects of pressure as a means to suppress the Peierls instability. Pressure is expected to reduce the electron-phonon coupling, which may be written in the form

$\lambda = J^2N(0)/K$, where $K = M\omega^2$ is the force constant.

The main effect of pressure is the increase of K due to a large Gruneisen constant and large compressibility of the external modes in the organic compounds[14]:

$-\partial \ln K/\partial \ln b = 20$, i.e., a 5% reduction in the intrachain lattice spacing b, obtained at a pressure of about 10-15 kbars, doubles K. Pressure also reduces the numerator in λ, but this effect is small, as verified by the variation of plasma frequency with pressure, so that the net effect of pressure is expected to be a reduction of λ.

4. THE $(TMTSF)_2X$ COMPOUNDS

As mentioned in the Introduction, the most apparent difference between the $(TMTSF)_2X$ compounds and the other organic metals is that the insulating state is a SDW state. Based on Fig. 1, this suggests the possibility that the superconducting state, obtained when the SDW is suppressed by pressure is a triplet state.[15] This is unlikely, because there is experimental evidence that the observed superconductivity is of the singlet type. Moreover, the triplet state is implied only by the oversimplified diagram obtained when retardation effects are neglected. We shall see that the latter modify the "g-ology" picture in a significant way leading to a possibility of crossover from SDW to SS type of order.

The second important new feature of the $(TMTSF)_2X$ compounds is that only the donor chains of the TMTSF molecules participate in the electron transport. The acceptor molecules are singly charged, the charge transfer being determined by stoichiometry. The acceptor molecules induce a static potential along the conducting donor chains of the form

$$W = \Delta \exp(i4k_F R_n) + \text{h.c.}, \qquad (3)$$

where R_n are the coordinates of the donor molecules. This induces a dimerization gap, Δ, and makes $4k_F$ a vector of the inverse lattice.

As a result, one can have an umklapp process in which two electrons on one side of the Fermi surface scatter together to the other side (Figure 3a).

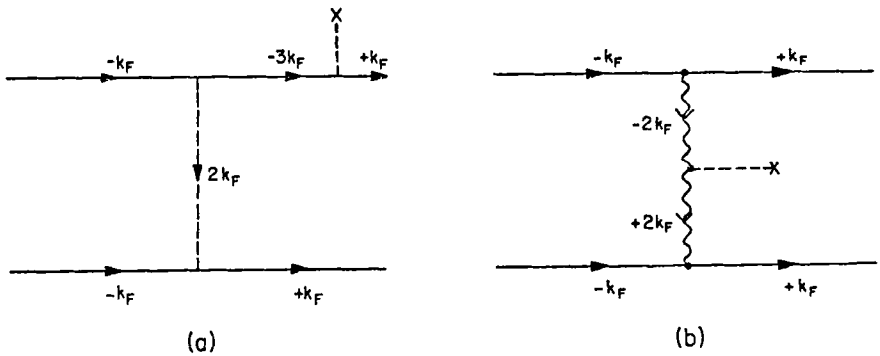

FIGURE 3. Umklapp scattering in presence of an external potential of period $4k_F$. a) non-retarded process involving electron scattering; b) retarded process via two phonons.

We denote this process by g_3 and its strength is related to g_1 by $g_3 = g_1(\Delta/E_F)$. An additional effect of the potential in eq. (3) is to add to the Hamiltonian a term which couples $2k_F$ and $-2k_F$ phonons[6]. The lowest order effect of this term is to provide an additional umklapp channel (Fig. 3b) in which an electron with momentum k_F emits a $2k_F$ phonon, this is Bragg scattered by the potential to a $-2k_F$ phonon, which is subsequently absorbed by another electron of momentum k_F. We denote this process by λ_3. Its strength is given by

$$\lambda_3 = |\lambda_1| \frac{8k_F^2 \Delta}{M\omega_o^2} \tag{4}$$

The main point is that λ_3 is a retarded interaction and depends strongly on pressure. Because of this strong pressure dependence, we feel that it plays an essential role for the understanding of these compounds.

5. THE g-OLOGY PICTURE REVISITED

Let us now extend the picture discussed in sections 2 and 3, and include in the Hamiltonian the retarded and nonretarded interactions, as well as the retarded umklapp process, λ_3, mentioned above[6]. The gap equations for the different instabilities are obtained from the lowest order irreducible self-energy diagrams, as in reference 11. The solution of these equations is particularly simple in the weak coupling limit, $\bar{g}_i$, λ_i, $<< 1$ and $T_c << \omega_o << E_c$ (where ω_o and E_c are the phonon energy and electron energy cutoffs, respectively). In this case the effect of the phonons is to replace the cutoff E_c by ω_o for the retarded interactions, resulting in a BCS like equations with two cutoffs

$$1 = \frac{-R}{2} \int_{-\omega_0}^{\omega_0} d\varepsilon \frac{\mathrm{tgh}(\varepsilon/2T_c)}{2\varepsilon} + \frac{-N}{2} \int_{-E_c}^{E_c} d\varepsilon \frac{\mathrm{tgh}(\varepsilon/2T_c)}{2\varepsilon} \tag{5}$$

where $\bar{g}^R$ and $\bar{g}^N$ are the effective coupling constants for the retarded and nonretarded interactions, and their values for the different phases are given in Table 1.

Table 1

	$\bar{g}^N$	$\bar{g}^R$
SS	$-\bar{g}_1 - \bar{g}_2$	$\lambda_1 + \lambda_2$
TS	$\bar{g}_1 - \bar{g}_2$	$-\lambda_1 + \lambda_2$
CDW	$-2\bar{g}_1 + \bar{g}_2 + 2\lambda_1 + 2\lambda_3$	$-\lambda_2 - \lambda_3$
SDW	$\bar{g}_2$	$-\lambda_2 + \lambda_3$

Note that the umklapp scattering affects only the CDW and SDW phases. The solution of eq. (5) is

$$T_c = \omega_0 \exp\{-[\tfrac{1}{2}g^R + \tfrac{1}{2}\frac{\bar{g}^N}{1-\frac{1}{2}\bar{g}^N \ln(E_c/\omega_0)}]^{-1}\} \qquad (6)$$

The effect of the different cutoffs for the retarded and nonretarded interactions is to reduce the coupling constants $\bar{g}^N$, exactly in the same way as the Coulomb interaction parameter μ is changed to μ^* in the usual expression for the superconducting T_c[16].

The phase diagram is again obtained by comparing T_c for the four instabilities. The result is shown in Figure 4, to lowest order in $\bar{g}^N \ln(E_c/\omega_0)$. The solid lines correspond to the case of $\lambda_3 = 0$. This phase diagram has a new feature compared to Fig. 1. The degeneracy of the point at the origin

at which all four phases coexist is lifted and one gets two points, A and B, at which three phases coexist. This implies that a SS-SDW coexistence boundary is now possible (the line AB in Fig. 4). In addition, there is a whole region of positive interactions to the right of the line $2\overline{g}_2 = \overline{g}_1$ in which superconductivity occurs. This is the consequence of retardation, exactly as in ordinary metals superconductivity is not excluded when $\mu > \lambda$, because one can still have $\mu^* < \lambda$.

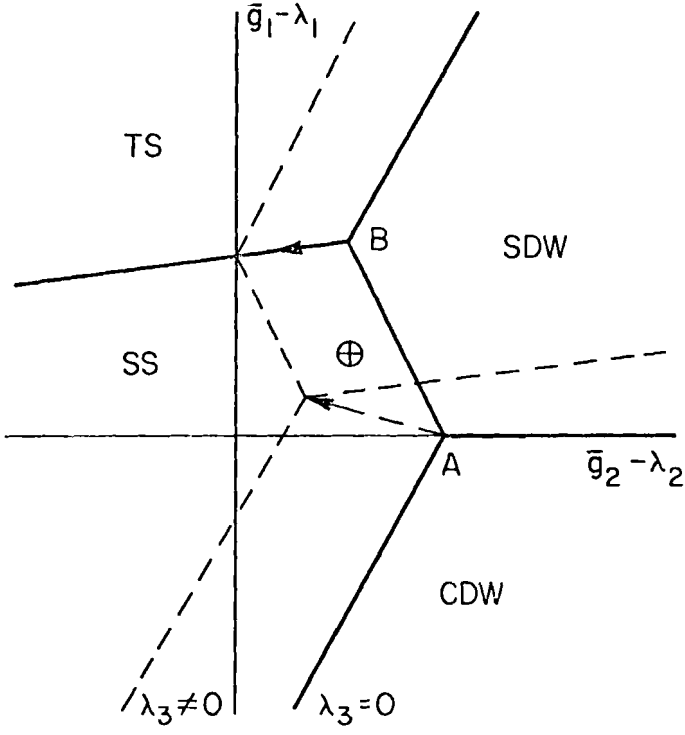

FIGURE 4. Phase diagram with retarded and nonretarded interactions. Full lines are the boundary lines for $\lambda_3 = 0$. Arrows indicate the motion of points A and B when λ_3 increases. The cross represents an assumed position of the compound.

Let us first assume that a compound is represented by a point in the SDW region to the right of the line AB. The main effect of pressure is most likely to reduce λ_1 and λ_2, so that such a point would move away from this line, and would not cross the line to the SS region. To explain such a behaviour it is necessary to take into account the umklapp process. When λ_3 increases the points A and B move as indicated by the arrows in Fig. 4, and the boundary between insulating and superconducting phases is shifted to the left. This happens also in the case of nonretarded interactions. It was shown both in the rigorous 1-d model[17] and in mean field theory[11] that in the presence of umklapp the line $2\bar{g}_2 - \bar{g}_1 = 0$ is replaced by $2\bar{g}_2 - \bar{g}_1 + \bar{g}_3 = 0$.

This behaviour explains the experimental results in the $(TMTSF)_2X$ compounds quite naturally. These compounds are presumably located somewhere at the position marked by the cross in Fig. 4. At ambient pressure they have a SDW ground state because $\lambda_3 \neq 0$. The main effect of pressure is to shift the AB line to the right until the system finds itself in the superconducting region. Since λ_3 appears in the exponent of T_{SDW} and λ_1 appears in the exponents of both T_{SDW} and T_{SS}, and both coupling constants decrease under pressure, we expect that both transition temperatures decrease with pressure. Since λ_3 is more sensitive to pressure than λ_1, we expect a stronger pressure dependence of T_{SDW} than of T_{SS}, which is consistent with the experiment:

$dT_{SS}/dP = -0.087\ ^{o}K/Kbar$ [3,4], and $dT_{SDW}/dP = -(1\text{-}2)\ ^{o}K/Kbar^2$

It was recently found[18] that $(TMTSF)_2ClO_4$ is superconducting at ambient pressure below 1.3 ^{o}K. The ClO_4^- ions appear to be disordered in this compound. A possible explanation along the lines of the present model, is that the disorder excludes the umklapp scattering and pressure is not necessary to suppress λ_3 in order to recover the favorable conditions for superconductivity.

In conclusion, we wish to point out that a qualitatively similar explanation for the SDW-SS crossover based on the

nonretarded g_3 term was recently suggested by Barisic et al.[19]

6. THE MEANING OF ONE-DIMENSIONALITY

Another possible explanation of the pressure effect in the $(TMTSF)_2X$ Compounds is that pressure increases the interchain coupling and thereby destroys the nesting of the Fermi surface and excludes the possibility of SDW's to form. If this were the case, the system would be effectively three-, or at least two-, dimensional. This point of view was promoted in ref. 4, who found that the anisotropy of the electric conductivity is strongly reduced under pressure, reaching a value of

$$\sigma_b(4.2^oK) \;/\; \sigma_a(4.2^oK) \simeq 7 \text{ at } 10 \text{ Kbar}.$$

However, there is experimental evidence that in spite of that, the nesting property is not destroyed. The authors of ref. 4 find a gap over most of the Fermi surface indicating the formation of density waves. We wish to point out that in the context of the present model, a system is "one-dimensional" as long as the nesting property is preserved, regardless of the value of $t_\perp$[9].

Recently, Kwak et al[20] observed Shubnikov-deHaas oscillations at 7.5 kbars in $(TMTSF)_2PF_6$, indicating electron and hole pockets of equal cross-sectional areas of less than 1% of the Brilloin Zone, and an effective mass close to m_e. Such pockets were observed and accounted for[21] in the two-chain compound HMTSF-TCNQ. They were also observed below the Peierls transition in the one-chain system $NbSe_3$ by transport methods.[22] Such pockets are expected in general in a two-chain system due to the deviations from a planar Fermi surface[20], and in monochain systems whenever there are deviations from perfect nesting of the Fermi surface, and the nesting vector $\underline{q}_o$ becomes a reciprocal lattice vector (in presence of CDW's or SDW's). In the latter case, the two sheets of the Fermi surface are almost equivalent, and shifting one of them by the nesting vector results in small electron

and hole pockets. It is reasonable to assume that in $(TMTSF)_2PF_6$, $q_o = (2k_F, \pi/b, q_c)$ (the value of q_c is less certain but irrelevant for the present argument), and that this vector at P = 7.5 kbars is still a reciprocal lattice vector due to the presence of SDW's[4]. This results in small banana-shape electron and hole pockets with a volume of the order of $(t_\perp/t_{\parallel})^2$ of the Brilloin zone.

To demonstrate this effect, we have taken the calculated shape of the cross-section of the Fermi surface in the (k_a, k_b)-plane for a particular set of parameters[23]. The electron and hole pockets resulting from shifting one sheet of the Fermi surface along the nesting vector are shown in Fig. 5.

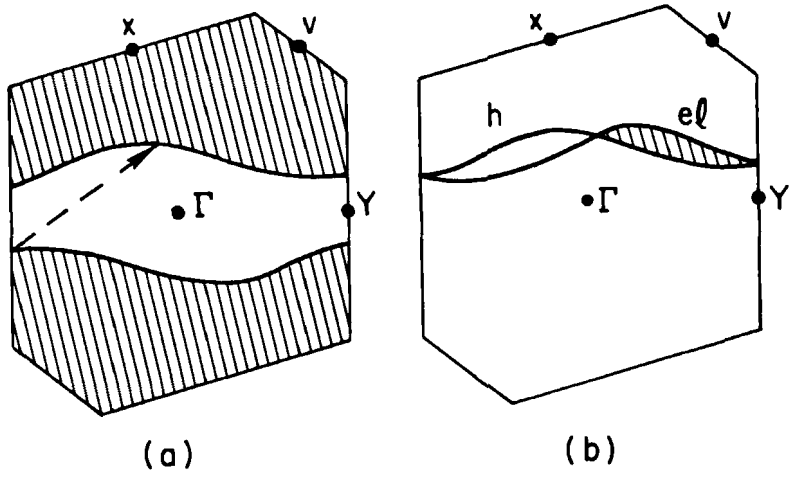

FIGURE 5 (a) Calculated cross-section of the Fermi surface of $(TMTSF)_2PF_6$ (ref. 23). Arrow indicates the nesting vector (approximate).
(b) Electron and hole pockets formed by shifting the lower section of the Fermi surface along the nesting vector.

To get these small pockets, a rather small anistropy (of the order of 0.1) is required, but the deviation from nesting at this anistropy is also small. Thus, the strong decrease under pressure in the anistropy of the electrical

conductivity accompanied by Shubnikov-deHaas oscillations is consistent with and supports the notion that the system we are dealing with is effectively "one-dimensional" with a very small deviation from the nesting property.

7. SUMMARY

We have shown that the discovery of the $(TMTSF)_2X$ Compounds requires some modifications in the "g-ology" picture which accompanied the field of one-dimensional metals since the beginning. In particular, the inclusion of retardation effects and umklapp scattering seems to be essential. When these are included, a simple and natural description of the behaviour of the $(TMTSF)_2X$ compounds is obtained.

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